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BULLETIN No. 1193

Washington, D. C. ▼ February 15, 1924

ESTIMATION OF COLLOIDAL MATERIAL IN SOILS BY ADSORPTION

By

P. L. GILE, in Charge, Soil Chemical Investigations; H. E. MIDDLETON, Scientist in Soil Physical Investigations; W. O. ROBINSON, W. H. FRY, and M. S. ANDERSON, Scientists in Soil Laboratory Investigations, Bureau of Soils.

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By P. L. Gile, *in Charge, Soil Chemical Investigations,* H. E. Middleton, *Scientist in Soil Physical Investigations,* W. O. Robinson, W. H. Fry, and M. S. Anderson, *Scientists in Soil Laboratory Investigations, Bureau of Soils.*

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INTRODUCTION.

This bulletin is a report of progress made in developing an adsorption method for determining the colloidal material in soils. It is anticipated that the method described can be improved as knowledge of the soil colloids is increased, but even in its present imperfect state it offers advantages over methods previously proposed and should, therefore, prove useful in soil investigations.

Many of the most important properties of soils in general and many of the special characteristics of particular soils are doubtless associated with the colloidal matter present. It has been shown in a previous publication that practically all the adsorptive power of a soil, for certain substances at least, is localized in the colloidal material (Anderson, *1*[1]). The colloidal material with its high adsorptive power probably, therefore, acts to a considerable extent as a regulator of the character of the soil solution, influencing the kind and concentration of the various bases in true solution and affecting the rate at which the soil minerals decompose. The plasticity (Davis, *6*) and coherence of soils are evidently functions of the colloidal matter or of some particular part of it. It has been generally recognized that part of the effects produced by different methods of cultivation and by the addition to the soil of various substances, such as lime, fertilizers, and manures, are to be attributed to the influence of these treatments on the condition of the colloidal matter present (Ehrenberg, *8*). In order properly to evaluate the part played by colloids in various soil phenomena, a method for determining the total quantity of colloidal material present is greatly needed.

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[1] Reference is made by number (italic) to "Literature cited," p. 39.

COLLOIDAL AND NONCOLLOIDAL SOIL PARTICLES.

A fairly sharp distinction can be made between material in true solution and that in colloidal suspension, but a sharp demarcation between colloidal material and that in a coarser state of subdivision is bound to be more or less arbitrary. The negative characteristics of colloidal material, slight influence on the boiling or freezing point of the dispersing medium, and hardly sensible osmotic pressure serve to differentiate colloidal suspensions from true solutions. The more positive characteristics of colloidal material, those associated with small size, such as the property of remaining in suspension in the dispersing medium, Brownian movement, and high adsorptive capacity are rather unsatisfactory criteria for a rigid separation of colloidal and larger particles.

The criterion of colloidal condition most generally adopted is that of size of the dispersed particles, the upper limit of colloidal particles usually being set at 0.1 micron.[2] The selection of exactly 0.1 micron as the upper limit of colloidal size is of course purely arbitrary. There are no grounds for assuming that the adsorptive power, Brownian movement, or reactivity of dispersed particles shows a sharp break at this particular point. Moreover, in the case of emulsoid colloids in the gel condition, the classification on the basis of size is not determinate. The division at 0.1 micron does, however, throw the colloidal particles into the submicroscopic region.

In the case of soil constituents, also, a rigid distinction can not be made between colloidal and noncolloidal material. Nevertheless, there will probably be little disagreement concerning the colloidality of most of the soil material which is classified as colloidal in this paper.

In the investigation described here all the organic matter of the soil is regarded as colloidal. A considerable part of the organic matter in normal soils can be readily peptized or dispersed into particles 0.3 micron or less in diameter, and the part of the organic matter which is not so readily dispersable—the less humified material, such as partially decomposed roots and plant residues—is doubtless just as strictly colloidal as the material in a more advanced stage of decomposition.[3] The celluloses and structural plant substances, as well as most of the intracellular material, is generally conceded to be of a colloidal nature, although in the dried state these substances can not readily be converted into the sol condition.

In this investigation all inorganic material was classified as colloid which could be dispersed into particles less than 1 micron in diameter without subjecting the soil to a drastic chemical or physical treatment that would disintegrate the mineral particles. One micron was selected as the upper limit for colloidal particles rather than the more conventional 0.1 micron, since a fairly sharp separation of particles can be made at 1 micron by subsidence or by centrifuging and the separation can readily be checked by microscopical observation. At 0.1 micron the control of size is inaccurate when dealing with mixtures of colloidal material, and a sharp separation by subsidence or centrifuging is exceedingly difficult. Soil particles 1 micron in diameter show a distinct Brownian movement, which is usually considered a colloidal characteristic. Also, some earlier investigators have used 1 to 2 microns as the upper limit of size of discrete "primary" or "ultimate" particles. It seems advisable, however, to place the limit of size for unaltered soil particles as low as can be accurately estimated, i. e., at 1 micron.

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[2] Freundlich (*10*, p. 2) selects 0.5 micron as the upper limit. On the other hand, many soil investigators have used 2 microns as the dividing line between colloid and noncolloid (Atterberg, *3*).

[3] An unextracted peat soil had just as high an adsorptive capacity for water as the material extracted from it, which was composed of particles less than 0.3 micron in diameter. The extracted colloid was slightly less adsorptive of ammonia and more adsorptive of malachite green than the unextracted peat.

The third kind of material classified as colloidal is that of certain aggregates or lumps of material which may occur in sizes up to 50 microns or even more in diameter. With the ultramicroscope it can be seen that these lumps are merely aggregates of small particles which are less than a micron in diameter. The constituent particles were not dispersable, however, by the methods we employed for this purpose. These lumps doubtless exist as such in the soil, although it is possible that they have been formed in some cases by the mechanical treatment adopted for fractionation of the soil.

Distinctly mineral particles which are larger than 1 micron in diameter are here treated as constituting the noncolloidal part of the soil.

PREVIOUS METHODS OF ESTIMATING THE COLLOIDAL MATERIAL IN SOILS.

The first to call particular attention to the colloidal matter in soils were Schloesing and Hilgard. Schloesing (*31, 32*) rubbed up clays and agricultural soils with considerable quantities of water, separated the coarser sands by decantation, treated the washings containing the finer soil particles with acid to dissolve $CaCO_3$, and then resuspended the fine material in water containing a little ammonia. The fine material from 5 grams of soil which remained in suspension for 24 hours in 2 liters of water he called "clay." He reported (*32*) 16 to 20 per cent of such material in heavy soils.

According to Schloesing (*33*, p. 476, and *34*, p. 67), this clay fraction, as well as a natural clay, contained two classes of substances: Very fine sands devoid of cohesion, and an amorphous substance, which he called "l'argile colloidale," that cemented the sand grains and was responsible for the plasticity of soils. This "colloidal clay" was very coherent, had a horny appearance, and was made up of formless (possibly submicroscopic) particles which would remain in suspension indefinitely. The colloidal clay was separated from the other material in the clay fraction by long-continued subsidence lasting several weeks or several months, with occasional decantations to get rid of noncolloidal clay which settled out. The separation of colloidal clay from the very fine sands was considered complete when, "le microscope ne permet plus de découvrir dans le liquide aucun élément figuré." (*34*, p. 67.) He stated that clays or soils contained very rarely more than 1.5 per cent of l'argile colloidale.

Schloesing's statement that the colloidal clay was free from other material when no shaped particles were visible microscopically showed that his argile colloidale was probably very similar to the colloid we separated by the supercentrifuge; at least his largest colloidal clay particles could not well have been smaller than the particles passing the supercentrifuge. Schloesing evidently based his conclusions concerning the small quantities of colloidal clay present in soils on the quantities he succeeded in isolating. His error, which has since been made by several other investigators, lay in assuming that his means of extraction and purification were substantially quantitative. As a matter of fact, he probably dispersed only part of the colloidal matter in his preliminary treatment of the soil and then lost colloid in the residues from which he repeatedly decanted.

About the same time as Schloesing, Hilgard (*16*) separated a "colloidal clay" from the soil. This colloidal clay he believed contained a "true clay substance," with a chemical composition similar to kaolinite, which was responsible for the plastic and adhesive properties of the soil. Hilgard classified as colloidal clay those particles that would "fail to settle in the course of 24 hours through a column of pure water 8 inches high" (*15*). He stated (*15* p. 333) that the percentage of this material "seems rarely to reach 75 in the purest natural clays, 40 to 47 in the heaviest of clay soils, and 10 to 20 in ordinary loams."

Apparently Hilgard believed that this fraction would contain, besides "the true clay substance," other colloidal material, such as ferric, silicic, and aluminic hydrates, which he assumed would impart no plasticity to soils. The material he obtained, however, seems to have had the same properties as that of Schloesing. Hilgard's method of extraction was possibly more thorough than that of Schloesing, but he doubtless included in his colloidal clay, particles that Schloesing graded out of his argile colloidale.

The very painstaking method of mechanical analysis reported by W. R. Williams in 1895 (*39*)was evidently somewhat more effective than that of Hilgard in extracting the colloidal matter of soils, in that the fractions of coarser soil particles were more thoroughly worked to rid them of colloidal material, and the method probably gave a more complete separation of colloidal and noncolloidal material.

The "schlamm" fraction secured by Williams, similar to the "clay" fraction of Hilgard, contained only those particles which would remain in suspension for 24 hours in a column of water 10 centimeters high. Williams stated that these particles, which were less than 1.5 microns in diameter, had very different properties from the larger particles. The schlamm material gave a good suspension of formless particles that showed an active Brownian movement. On drying, the material shrank greatly, becoming a horny mass of conchoidal fracture that would adhere strongly to the tongue. Williams attributed the coherence, plasticity, and adsorptive power of soils to the schlamm material, and stated that this material constituted 1.5 per cent to 40 per cent of the soil (*39* p. 301).

The materials isolated by Schloesing, Hilgard, and Williams were evidently all about the same and were chiefly colloidal. Apparently, Ehrenberg (*8* p. 99) does not recognize this, as in his recent compendium of colloidal phenomena in soils he agrees with Schloesing that soils contain only 0.5 per cent to 1.5 per cent of colloidal clay. Ehrenberg evidently labors under the same misconception as Schloesing in believing that the material which remains longest in suspension differs essentially from material which does not remain so long in suspension.

The chief object of much of the earlier work, in which colloidal material was isolated from the other soil constituents, was not to make a determination of all the colloidal material present in the soil, but merely to separate the soil into different-sized particles. It was, however, clearly recognized by Hilgard and Williams that one of the chief problems in such a separation was the disintegration of lumps of material into the individual particles of which they were formed. The basis of the separation was entirely one of size.

As a matter of fact, under normal moisture conditions probably no soil contains more than a trace of colloidal material in the sol condition. The colloidal material must be virtually all in a coagulated or gel form, since there is not sufficient water present to form a disperse medium. The problem of separating the colloidal material by a method of mechanical analysis, therefore, becomes largely one of converting the colloidal material from the gel to the sol form. Since a considerable part of the gels in most soils is in a more or less indurated condition that is difficultly dispersable, it might be expected that the exact character of the suspension obtained, its stability, and the size of the particles would be a more or less fortuitous matter, depending on the means of dispersion employed. This seems especially probable from a consideration of the well-known coagulating, peptizing, and stabilizing effects of various concentrations of different ions.

From this point of view, the ideas of Schloesing and Ehrenberg, that the particular preparations they obtained represented the only truly colloidal matter in the soil, appear illogical. It is of course true that size is one of the most dependable criteria for colloids, but in the case of many preparations the question arises, size of what? In the case of a coagulated suspensoid colloid, such as colloidal gold, the size of the floccules is not the criterion, but the size of the individual particles that are coagulated. But in the case of coagulated emulsoid colloids or of partially dehydrated emulsoid gels, structure or size of the molecular aggregates is evidently the criterion, and size in this case can not be determined by direct observation.

In recent years a number of rapid methods have been proposed for estimating the comparative amounts of colloids in soils. Many of these methods are based on the fundamental misconception that by some simple treatment of the soil, such as by mere agitation with water, all the colloidal matter, or some definite part of it, is at once brought into suspension. Among such methods may be mentioned the method of Sokol (*35*) based on the relative volumes occupied by the colloid when first it is flocculated and when it has settled for 24 hours; and the method of Scales and Marsh (*30*) based on the turbidity of the suspension obtained on shaking the soil for five minutes with distilled water.

These methods fail to take into account that the quantity of colloidal matter brought into suspension by mere agitation of a soil with water may vary greatly according to a transitory condition of the soil. Our experience shows that some soils yield practically no colloidal matter on the first agitation with water, but after decantation of the water a second treatment yields a heavy colloidal suspension. In such cases the first treatment with water doubtless removes a certain amount of a soluble salt which has a flocculating effect. König and Hasenbäumer (*17*) showed that after addition of aluminum chloride to a soil, agitation with ten fresh portions of water failed to bring any colloid into suspension; but the eleventh treatment with water containing a small amount of ammonia produced a heavy suspension.

Other methods which are based on adsorption—a positive property of the colloids—have been proposed for indicating the relative colloidal contents of soils. Ashley's method (*2*), involving a determination of the quantity of malachite green adsorbed, has been most widely used on ceramic clays, which may be regarded as a special type of soil. Our results show, however, that while Ashley's method might indicate differences in the plasticities of ceramic clays, it does not indicate the relative colloidal contents of agricultural soils, since the colloids extracted from different soils vary greatly in their adsorptive capacities for this dye.

Mitscherlich (*21*, p. 476) has suggested that the amount of water vapor adsorbed by soils under standard conditions is probably to be attributed almost entirely to the colloidal matter present, but that the water adsorption values of different soils probably do not indicate the relative amounts of colloids present, since different soils contain different colloids which vary in their adsorptive capacities. Our results would indicate that while colloids extracted from different soils may vary considerably in their adsorptive capacities for water vapor when in equilibrium with the partial pressure of water vapor afforded by 10 per cent sulphuric acid they have a relatively constant adsorptive capacity when in equilibrium with 3.3 per cent sulphuric acid.

Stremme and Aarnio (*36*) applied the Van Bemmelen method of determining colloids by digestion with sulphuric and hydrochloric acids to various rocks, and they concluded that the method was subject to error in that certain noncolloidal minerals were dissolved.

Van der Leeden and Schneider (*18*) conclude that the dye adsorptions of soils do not correspond to the colloidal contents, that unweathered silicates as well as colloidal material are dissolved by digestion of the soil with hydrochloric acid, and that there is not an exact parallelism between the quantities of water and dye adsorbed by soils.

Tempany (*37*) has recently proposed that the colloidal content of a soil might be estimated from the shrinkage of the soil on drying. It is yet to be proved, however, that the colloidal materials in all soils have the same shrinkage coefficient.

In the earlier investigations, and in much of the modern work, the attempt has been made to determine the colloidal matter in soils through the methods of mechanical analysis; that is, by actual separation of the colloidal and noncolloidal soil constituents. Proceeding in this manner, it was, of course, necessary to get the colloidal matter in suspension before it could be recognized as colloid and size of the particles became the sole criterion of judging what was colloid.

Such a separation would be definite and entirely satisfactory for the interpretation of soil phenomena if all the soil particles were of one kind; that is, if the particles were all fragments of crystalline minerals differing only in size. The uncertainty of such separations and the unsatisfactoriness of the results obtained are due to the presence of colloidal material which it is difficult to disperse into discrete particles of any definite size. A determination of the colloidal material in soils is, therefore, needed to supplement the results afforded by any system of mechanical analysis based on size alone, which does not disperse colloidal aggregates (Davis, *7*).[4]

ADSORPTION METHOD OF ESTIMATING COLLOIDAL MATERIAL IN SOILS.

DESCRIPTION OF METHOD.

The earlier investigators in estimating the colloidal material in soils actually isolated at least a part of the colloids, but they did not utilize the marked adsorptive properties of the material as a means of characterization nor as a test for complete separation. Later investigators recognized high adsorptive capacity as a distinguishing characteristic of the colloidal material, but failed to isolate the material. Knowing the adsorptive capacity of the kind of colloidal material present in a given soil and the adsorptive capacity of the whole soil, one should be able to estimate the quantity of colloidal material present. If the adsorptive power of the soil is due wholly to the colloidal material, the ratio,

$$\frac{\text{adsorption per gram of soil}}{\text{adsorption per gram of colloid}} \times 100$$

should give the percentage of colloidal material in the soil.

Moore, Fry, and Middleton, of this Bureau (*22*), suggested this method of estimating the colloidal material in soils. They determined the adsorption ratio in the case of one soil, measuring the quantities of malachite green and ammonia gas adsorbed by the soil and by a sample of colloidal material extracted from the soil. The adsorption ratio obtained by malachite green agreed exactly with the ratio obtained by ammonia.

It might seem that adsorption by noncolloidal soil particles would constitute a fundamental error in this method, making the ratio of the adsorptive capacities of soil and colloid indicate a higher percentage of colloid in the soil than was actually present. However, a subsequent investigation (Anderson, *1*) showed that in the case of ordinary soils more than 95 per cent of the total adsorptive capacity of the soil for malachite green, water, and ammonia is located in the colloidal constituents. Only in the case of highly micaceous soils is the adsorption by noncolloidal particles significant.

Since the adsorption method of determining the colloidal content of a soil would not, as a rule, be seriously affected by noncolloidal constituents, it seemed advisable to try the method on a number of different soils, 32 in all. It also seemed advisable to determine the adsorptive capacities of the soils and colloids for water vapor as well as for malachite green and ammonia. Theoretically, any substance which is not appreciably adsorbed or acted upon by the noncolloidal soil particles, but which is adsorbed by the colloidal material, might be used for determining the colloidal content of the soil by this method.

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[4] It is doubtful if the method of mechanical analysis proposed by Sven Odén (*23*, *24*) attains as complete a deflocculation of the colloidal material as the older method of Williams, since the residues apparently are not "worked" to the same extent.

It was expected that some evidence concerning the reliability of the method would be afforded by the closeness with which the ratios,

$$\frac{\text{adsorption per gram of soil}}{\text{adsorption per gram of colloid}}$$

obtained by the adsorptions of dye, water, and ammonia agreed with each other.

EXPERIMENTAL PROCEDURE.

SOILS USED.

The soils selected for a trial of the proposed method of colloid determination were some of the most important agricultural types. They varied in texture from sands to such heavy clays as the Sharkey clay and the Stockton clay adobe soils. In most cases the surface soil represented the first 8 to 12 inches of material and the subsoil samples were taken to a depth of 2 to 3 feet. The samples were received in a fairly moist condition and were kept moist until ready for use, since in previous work there had been some evidence that thorough drying was likely to make extraction of the colloid more difficult. M. H. Lapham, J. E. Lapham, and W. Edward Hearn of The Soil Survey collected the samples.

ISOLATION OF A SAMPLE OF THE COLLOIDAL MATERIAL.

No attempt was made in the first part of the work described here to extract all the colloidal matter in the soils. The idea was to isolate from each soil enough of the colloidal material for chemical analysis and for determination of the adsorptive capacity for malachite green, water vapor, and ammonia gas. The samples of colloid for the determination reported in Table 1 were extracted virtually as described in the preliminary paper by Moore, Fry, and Middleton (*22*), although in the subsequent work this procedure was altered somewhat.

One hundred pounds of each soil were agitated in barrel churns with 500 pounds of distilled water for two hours. After standing for 18 hours the turbid liquid was siphoned off and the soil was again agitated with water to obtain a further yield of suspended matter. Frequently the second treatment of the soil gave a heavier suspension than the first, although a few soils failed to give any appreciable quantity of suspended matter on three such treatments. In such cases a fourth treatment with water containing approximately 1 part of ammonia to 3,000 parts of water was very effective in producing a suspension. The turbid extract from the soils was run through a high power centrifuge (known in the trade as a supercentrifuge) driven at the rate of 17,000 revolutions per minute, which threw out a large part of the suspended matter. In this process the particles were exposed to a force of approximately 17,000 gravity for about 3 minutes.

The colloidal suspension which passed through the centrifuge was first concentrated by sucking the water off through batteries of Chamberland-Pasteur filters (bogie F), the colloidal matter collecting on the outside of the filters.[5] When the colloidal matter had thus been concentrated in a moderate volume of water it was taken down to a nearly air-dry condition on the steam bath. The amount of colloid thus isolated amounted to about 1 per cent of the weight of the whole soil.

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[5] The slimy film of colloid which collected on the outside of the filters was readily removed from time to time by releasing the suction and blowing air into the tubes.

Samples were taken for the adsorption of malachite green when the material had reached a thin, pasty condition,[6] while the water adsorption was determined on the air-dried material and the ammonia adsorption on the material dried at 110° F.

Suspensions of colloidal material which passed through the supercentrifuge were examined microscopically. Practically no particles were visible in the ordinary microscope. Examination was also made, using a 3-millimeter objective, 12.5 X eyepiece, and a dark field illumination. Under these conditions the apparent size of the particles seldom exceeded 0.3 micron in diameter.[7] The unaggregated particles had a most active Brownian movement and were readily coagulated by electrolytes. The suspended matter in most cases did not settle out appreciably on standing for many months.

As the concentrated colloidal material was dried, it shrank greatly, finally becoming a horny or resinlike mass that had a conchoidal fracture. It would polish readily and adhere strongly to the tongue. This material was doubtless just as pronouncedly colloidal as that extracted by Schloesing (*34*) or that described by Ehrenberg (*8*, p. 102). It also seemed to have the same properties as the materials described by Hilgard (*16*) and by Williams (*39*).

METHODS OF DETERMINING QUANTITIES OF MALACHITE GREEN, WATER, AND AMMONIA ADSORBED.

The adsorption of malachite green was determined as follows: Approximately 0.25 gram of colloid or 1 gram of soil was shaken over night with 25 cubic centimeters of water in an end-over-end shaker. Enough N/10 sodium oxalate was then added to precipitate any soluble calcium present. After shaking for 15 minutes, a 0.2 per cent solution of malachite green oxalate was added, with repeated shaking until the depth of color in the supernatant liquid was about the same as that of a check solution containing 0.0004 gram dye per cubic centimeter. Shaking was continued for 1 hour to insure complete adsorption. About 5 cubic centimeters of normal sodium chloride solution was then added to coagulate the colloid, and after centrifuging to throw down the coagulated material, the supernatant liquid was read colorimetrically against the check solution. The quantity of dye adsorbed was calculated from the amount added and the amount left unadsorbed.

The determinations reported in Table 1 were all made on the moist colloid and on the air-dried soil. Several tests showed that the 18-hour shaking of the sample preliminary to determining the adsorption was needed to bring the material in the most adsorptive condition. This was particularly important in the case of soils. Duplicate determinations made by this method usually agreed well, variations between different determinations averaging about 5 per cent of the values obtained.

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[6] In subsequent work reported here the air-dried colloidal material was used for determining the adsorption of malachite green.

[7] Of course, some aggregates of larger size were seen, but these were susceptible of resolution into particles of the size mentioned. Part of the material may well have been invisible. This refers not only to exceedingly small particles, but also to colorless particles of any size which had a refractive index sufficiently near that of water.

In determining the adsorption of ammonia, 5 to 10 gram samples of soil or 2 to 5 gram samples of colloid which had previously been dried for 18 hours at 110° C. were used. The sample was placed in a U-tube which was evacuated for 15 minutes while immersed in boiling water. After replacing the boiling water about the U-tube by an ice-pack, ammonia gas was let into the U-tube through a drying train for two to four hours. The pressure of ammonia gas during this time was maintained at 1 centimeter above that of the atmosphere by a mercury manometer. When the mercury level in the manometer remained without perceptible change for 30 minutes with the ammonia cut off, the adsorption was regarded as complete. Two bottles containing a saturated solution of boric acid were then attached to the U-tube, the ice-pack was removed, the pressure in the apparatus was kept reduced by about 10 centimeters of mercury in the manometer by means of a filter pump, air was let in through a soda-lime tower, and boiling water was again placed around the U-tube. In this way all the ammonia was swept out of the apparatus within 30 to 40 minutes. The ammonia in the boric acid solution was titrated, using methyl orange as an indicator. The quantity of ammonia thus obtained was corrected for the blank of unadsorbed ammonia in the apparatus. This method gave the amount of ammonia adsorbed at 0° C. which was driven off at 100° C. Variations in duplicate determinations by this method were usually not greater than 3 per cent of the values obtained.

The adsorption of water vapor was determined as follows: About 2 grams of colloid or 2 to 4 grams of soil, previously air dried and passed through a 100-mesh sieve, were weighed into shallow weighing bottles. The uncovered weighing bottles were placed in a desiccator containing a large amount of 3.3 per cent sulphuric acid, and the desiccator was then evacuated to 50 millimeters or less of mercury. The desiccator was kept in a thermostat maintained at 30° C. for five days; at the end of which time the adsorption of water vapor was practically complete. The samples were then weighed moist and weighed again after drying for 18 hours at 110° C. The difference between the two weights represented the quantity of water adsorbed by the sample. A more detailed description of the procedure is given in a previous paper (Robinson, *26*).

The adsorption of the soil and of the corresponding colloid were determined in the same run. Under these conditions duplicate determinations usually agreed within 2 per cent of the values obtained. Duplicate determinations made in different runs might show considerably larger variations.

EXPERIMENTAL RESULTS.

THE ADSORPTIVE CAPACITIES OF SOILS AND EXTRACTED COLLOIDAL MATERIAL.

The adsorptive capacities of 32 soils and of samples of the colloidal matter extracted from these soils are given in Table 1. In each case the adsorptive capacity is expressed as the weight of dye, water, or ammonia adsorbed by 1 gram of the material.

TABLE 1.—*Adsorption of malachite green, water, and ammonia by soils and soil colloids.*

Type of soil or colloidal material.	Adsorbed per gram of soil.			Adsorbed per gram of colloidal material.		
	Dye.	H_2O.	NH_3.	Dye.	H_2O.	NH_3.
	Gram.	*Gram.*	*Gram.*	*Gram.*	*Gram.*	*Gram.*
Carrington loam:						
Soil	0.0531	0.1005	0.0168	0.2744	0.3102	0.0523
Subsoil	.0504	.0978	.0170	.3210	.3327	.0665
Cecil clay loam:						
Soil	.0078	.0341	.0034	.0770	.3359	.0230
Subsoil	.0402	.0903	.0050	.1582	.2870	.0192
Chester loam:						
Soil	.0148	.0203	.0049	.1348	.2398	.0293
Subsoil	.0239	.0676	.0087	.1392	.2723	.0256
Clarksville silt loam:						
Soil	.0353	.0789	.0077	.1424	.3390	.0359
Subsoil	.0506	.0804	.0106	.2154	.3147	.0408
Hagerstown loam:						
Soil	.0213	.0434	.0066	.1584	.2592	.0278
Subsoil	.0314	.0857	.0089	.1704	.2675	.0299
Huntington loam:						
Soil	.0236	.0632	.0104	.1750	.2739	.0319
Subsoil	.0182	.0604	.0083	.1538	.2903	.0274
Manor loam:						
Soil	.0188	.0520	.0064	.1640	.2822	.0308
Subsoil	.0223	.0632	.0057	.1838	.3402	.0264
Marshall silt loam:						
Soil	.0782	.0803	.0180	.2978	.2940	.0536
Subsoil	.1049	.1030	.0212	.3076	.3000	.0568
Miami silty clay loam:						
Soil	.0322	.0685	.0103	.2134	.3020	.0411
Subsoil	.1148	.1540	.0194	.2096	.3075	.0358
Norfolk fine sandy loam:						
Soil	.0167	.0261	.0055	.1464	.2430	.0303
Subsoil	.0275	.0565	.0055	.1158	.2755	.0295
Ontario loam:						
Soil	.0312	.0424	.0070	.1968	.2289	.0379
Subsoil	.0231	.0365	.0064	.1932	.3203	.0387
Orangeburg fine sandy loam:						
Soil	.0084	.0164	.0025	.1138	.2630	.0411
Subsoil	.0268	.0655	.0059	.1624	.3045	.0363
Sassafras silt loam:						
Soil	.0271	.0212	.0047	.1996	.2659	.0329
Subsoil	.0289	.0586	.0074	.2188	.3097	.0340
Sharkey clay, soil	.2128	.1886	.0358	.3757	.3080	.0609
Stockton clay adobe:						
Soil	.2075	.1471	.0320	.4128	.3410	.0617
Subsoil	.0644	.0785	.0189	.4308	.3365	.0560
Vega Baja clay loam, soil	.0369	.1805	.0147	.0584	.3125	.0206
Wabash silt loam:						
Soil	.1088	.0990	.0212	.3698	.3325	.0614
Subsoil	.1050	.1002	.0207	.3866	.3090	.0344

The adsorptive capacities of the different soils for all three substances—malachite green, water, and ammonia—varied greatly. This was to be expected, since the adsorption of the soil is conditioned by the kind of colloidal matter as well as by the quantity present.

The adsorptive capacities of the samples of colloidal matter extracted from the different soils are of considerable interest. The following facts seem especially significant: There are wide variations in the adsorptive capacities of the different colloidal materials for malachite green and for ammonia, but the adsorptive capacities of the different colloids for water vapor are more nearly constant. The highest and lowest values for malachite green are 0.4308 and 0.0584; the extremes for ammonia are 0.0665 and 0.0192; whereas the extremes for water are 0.3410 and 0.2289. The relative constancy of the adsorptive capacities of the different colloidal materials for water vapor suggested the possibility of obtaining an indication of the colloidal content of soils by merely dividing the water adsorptive capacity of a soil by 0.298 which was the average water-adsorptive capacity of the different colloids tested (Robinson, *26*). It should be noted, however, that this relative constancy in the water-adsorption values of the different colloids may well hold only for the particular conditions of the method used. Preliminary work indicates that greater variations may be expected to occur in the water adsorption values of the different colloids when the materials are in equilibrium with the vapor pressure of water afforded by 10 per cent sulphuric acid.

There is only a general parallelism between the quantities of malachite green, water vapor, and ammonia adsorbed by the different colloidal materials. The colloids of the Sharkey soil and of the Stockton, Wabash, Carrington, and Marshall soils and subsoils fall into one group, the least adsorptive member of which has an appreciably higher adsorptive capacity for dye or for ammonia than any of the other colloids. However, many of the other samples of colloidal material differ widely in their adsorptive capacities for these two substances. The much smaller variations in the adsorptive capacities for water vapor show practically no correspondence to the variations in the adsorptive capacities for dye or for ammonia.

This lack of correspondence in the adsorptive capacities of the colloids for malachite green, water, and ammonia is similar to that observed in the adsorptions by mineral powders and by synthetic inorganic gels, reported in a previous publication (Anderson, *1*). The silica gel, for example, which was highly adsorptive of ammonia, adsorbed practically no dye. Thus far we have obtained very little indication of any correspondence between the empirical chemical compositions of the colloidal materials and their adsorptive capacities for the three substances.

It is an interesting fact that the colloid of nearly every subsoil has an adsorptive capacity for malachite green, water or ammonia which is almost the same as that of the corresponding surface soil. The only marked exceptions to this generalization occur in the adsorption of dye by the Clarksville, Orangeburg, and Wabash colloids and in the adsorption of water by the Ontario colloid. This similarity in adsorptive capacities would indicate that the colloidal material in the subsoil is in most cases very nearly the same as that occurring in the surface soil. The adsorption evidence is particularly strong on this point, inasmuch as the adsorptive capacity of any one colloid for malachite green shows little correspondence to its adsorptive capacity for water or ammonia. The surface and subsoil colloids also seem to be very nearly alike in their ultimate chemical composition. (Robinson and Holmes, *27*.)

PERCENTAGES OF COLLOIDAL MATERIAL INDICATED BY THE ADSORPTION METHOD.

As already pointed out, the relative adsorptive capacities of the soil and of the corresponding colloid should indicate the quantity of colloidal material present in the soil, inasmuch as practically all the adsorptive capacity of a soil seems to be due to the colloidal material. From the data given in Table 1 the adsorption ratios

$$\frac{\text{adsorption per gram soil}}{\text{adsorption per gram colloid}}$$

have been calculated for the different soils. The percentages of colloidal material present in the soils as indicated by the adsorptions of dye, water, and ammonia (ratio × 100) are given in Table 2.

TABLE 2.—*Colloidal content of soils calculated by dye, water, and ammonia adsorption ratios.*

Type of soil.	Colloidal material in soil indicated by adsorption ratios, substance adsorbed being—		
	Dye.	H_2O.	NH_3.
	Per cent.	*Per cent.*	*Per cent.*
Carrington loam:			
Soil	19.4	32.4	32.1
Subsoil	15.7	29.4	25.6
Cecil clay loam:			
Soil	10.1	10.2	14.8
Subsoil	25.4	31.5	26.0
Chester loam:			
Soil	11.0	8.5	16.7
Subsoil	17.2	24.8	34.0
Clarksville silt loam:			
Soil	24.8	23.3	21.4
Subsoil	23.5	25.5	26.0
Hagerstown loam:			
Soil	13.4	16.7	23.7
Subsoil	18.4	32.0	29.8
Huntington loam:			
Soil	13.5	23.1	32.6
Subsoil	11.8	20.8	30.3
Manor loam:			
Soil	11.5	18.4	20.8
Subsoil	12.1	18.6	21.6
Marshall silt loam:			
Soil	26.3	27.3	33.6
Subsoil	34.1	34.3	37.3
Miami silty clay loam:			
Soil	15.1	22.7	25.1
Subsoil	54.8	50.1	54.2
Norfolk fine sandy loam:			
Soil	11.4	10.7	18.2
Subsoil	23.7	20.5	18.6
Ontario loam:			
Soil	15.9	18.5	18.5
Subsoil	12.0	11.4	16.5
Orangeburg fine sandy loam:			
Soil	7.4	6.2	6.1
Subsoil	16.5	21.5	16.3
Sassafras silt loam:			
Soil	13.6	8.0	14.3
Subsoil	13.2	18.9	21.8
Sharkey clay, soil	56.6	61.2	58.8
Stockton clay adobe:			
Soil	50.3	43.1	51.9
Subsoil	14.9	23.3	33.8
Vega Baja clay loam, soil	63.2	57.8	71.4
Wabash silt loam:			
Soil	29.4	29.8	34.5
Subsoil	27.2	32.4	32.1

The dye, water, and ammonia adsorption ratios all substantially agree as to the quantity of colloidal material present in the 13 following soils: Cecil subsoil, Clarksville soil and subsoil, Marshall subsoil, Miami subsoil, Norfolk subsoil, Ontario soil, Orangeburg soil, Sharkey soil, Stockton soil, Vega Baja soil and Wabash soil and subsoil. In the case of these soils the differences in the percentages of colloidal material calculated from the adsorption of the three subtances are about what would be produced by usual variations in individual adsorption determinations.

In the case of five soils—Chester subsoil, Hagerstown soil, Huntington soil and subsoil, and Stockton subsoil—widely different percentages of colloidal matter are indicated by the adsorptions of all three substances, malachite green, water, and ammonia.

In the case of the remaining 14 soils there is a good agreement between the quantities of colloidal matter indicated by the adsorptions of some two of the substances, but the adsorption of the third substance indicates a percentage of colloidal matter one-third to one-half higher or lower than the other two.

It will be noted that where there is a marked disagreement between all three adsorption ratios the dye ratio invariably shows the lowest percentage of colloidal matter and the ammonia ratio the highest percentage, the water ratio giving a mean value. Also, in those cases where two of the ratios agree and the third disagrees, the ammonia ratio is usually the highest and the dye ratio the lowest. Thus there seems to be a certain regularity in the disagreements.

CAUSES OF DISCORDANT RESULTS.

POSSIBLE ERRORS IN THE METHOD.

Considering the results as a whole, it seems apparent that the adsorption ratio of soil and sample of colloidal material must give at least an approximate idea of the colloidal content of a soil. The many close agreements between the ratios afforded by the adsorptions of such widely different substances as malachite green, water, and ammonia can hardly be conceived of as due to chance. On the other hand, the occasional wide disagreements between the ratios calculated from the adsorptions of the different substances indicate that some important factor or factors influencing the relative adsorptions of the soils and colloids have not been taken into consideration in the methods employed.

The changes which are supposed to take place in the colloidal matter of the soil on drying, moistening, freezing, etc., might, in the case of certain soils, have influenced the ratios. Beaumont (*4*) found that the water-adsorptive capacity of a soil was considerably reduced by drying at 110° C., and we found that the adsorptive capacities of several colloids for dye and water were reduced by about 7 per cent through heating to 110° C. Such effects may be very pronounced in freshly prepared colloids.

In the case of freshly prepared colloids the phenomenon generally known as "aging" markedly influences the character and adsorptive capacity of the material (Van Bemmelen, *5;* Freundlich and Schucht, *12;* Freundlich and Hase, *11*). We found that the adsorptive capacities of silicic acid, "aluminum silicate," iron hydroxide, and aluminum hydroxide gels for malachite green, water, and ammonia varied greatly with the age of the material. In the case of soil colloids, however, aging, if operative at all, probably would not be marked inasmuch as the material must be in approximate equilibrium with the general soil conditions to which it is exposed. While we have not observed alterations in the adsorptive capacities of soils comparable to those taking place in freshly prepared gels, a few soils were found which changed appreciably in their adsorptive capacity for malachite green when kept for several months in an air-dried condition. Many other soils tested remained sensibly constant in their adsorptive capacity when kept air-dried for more than a year.

It is possible that some of the ratios given in Table 2 may be inaccurate as determinations of the percentage of colloidal material in the soil owing to unequal changes taking place, previously to testing, in the adsorptive capacities of the soil and the extracted colloidal material. This, however, could not be an error of very general occurrence. Many duplicate determinations of the water-adsorption ratios made at wide intervals checked well. Miscellaneous data obtained indicate that if such changes do take place they are most likely to affect the adsorption of dye.

There are, however, two general elements of uncertainty in measuring the colloidal content of the soil from the relative adsorptive capacities of the soil and sample of colloidal material. It is of course assumed in this method of calculation that the adsorptive capacity of the colloidal matter isolated from the soil is not altered during the process of isolation and preparation of the material. In other words, it is assumed that the sample of colloidal material as prepared has the same power of adsorption that it has when present in the untreated soil. If this assumption is not entirely correct in the case of all the colloidal materials, if certain colloids after extraction are more adsorptive of malachite green and less adsorptive of ammonia than they are in the unextracted soil, it might explain the disagreement of certain ratios.

Another general cause for disagreement in certain of the ratios may lie in the samples of colloidal material. The different kinds of colloids[8] making up the colloidal material extracted from a soil must have widely different adsorptive capacities for malachite green, also for ammonia, and to a much less extent for water. This seems evident from the variations in the adsorptive capacities of the colloidal materials extracted from different soils reported in Table 1 and from tests made of the adsorptive capacities of artificial inorganic gels. The ratio of adsorption of soil to adsorption of colloid would, therefore, represent the percentage of colloidal material in the soil only when the sample of colloidal matter extracted was truly representative, with respect to adsorptive capacity at least, of all the colloidal material in the soil. If the sample of colloidal material was not representative, the dye, water, and ammonia adsorption ratios would not be expected to agree. Since the results shown in Table 2 are based on samples which were probably only a tenth to a twentieth part of all the colloidal material in the soil, it might be expected that in many instances the samples were not representative.

These two most probable sources of error in the adsorption method of determining colloids—the lack of representativeness of the sample of colloidal material and possible alteration in adsorptive capacity of the colloid produced by extraction—are discussed in the following.

REPRESENTATIVENESS OF A SAMPLE OF COLLOIDAL MATERIAL.

Plan of investigation.—Since the colloidal material in any one soil appears to be a mixture of at least several different colloids, which presumably would vary considerably in the stability of their suspensions and in the readiness with which they are redispersed after coagulation, it might be expected that a small sample of colloidal material extracted from a soil would be composed only of those colloids which disperse most readily and would not, therefore, be at all representative of the remainder of the colloidal material in the soil. This is assuming, however, that a mixture of the soil colloids is readily separated into its constituents. As a matter of fact, attempts at separation of the colloidal constituents by various means indicated that this separation is not readily brought about.

A direct comparison between a small sample of colloidal material and all the colloidal material in the soil could not be obtained, since it was impossible with the means we employed to extract all the colloid present. However, a small sample of the extractable colloid could be compared with all the extractable colloid. In order to do this and at the same time to gain information concerning the uniformity of the extractable colloidal material in soils, small lots of colloidal material were successively extracted from the same soil and the adsorptive capacities of the different lots compared.

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[8] "Different" colloids here is intended to include different states, as of aging or dispersion, of the same chemical substance as well as substances of a different chemical composition.

An indirect comparison was also obtained between the adsorptive capacities of the extractable and unextractable colloidal material in a manner which will be described in detail further on, but which was essentially as follows: All colloid possible was extracted from the soil and the residual soil material was quantitatively recovered. The quantity of unextracted colloid remaining in the soil residue was determined microscopically. The adsorptive capacity of the residue was also determined and the quantity of colloid present calculated by the ratio,

$$\frac{\text{adsorption per gram of residue}}{\text{adsorption per gram of extracted colloid}}$$

A comparison between the quantity of colloid determined microscopically and the quantity of colloid indicated by the adsorption ratios was virtually a comparison between the adsorptive capacities of the extractable and unextractable colloids.

Comparison of successive samples of extractable colloidal materials.—In order to determine how closely a small sample of colloidal material represented the rest of the extractable colloid, successive extractions of colloidal material were made from the following five soils: Sassafras and Huntington subsoils, and Marshall, Sharkey, and Vega Baja soils. The dye, water, and ammonia adsorption ratios all indicated widely different percentages of colloid material in the first two soils. The dye adsorption ratio was very different from the water and ammonia ratios in the case of the Marshall soil, while in the case of the Sharkey and Vega Baja soils, there was a fair agreement between all three ratios. If sampling of the colloidal material was the controlling factor affecting the agreement of the different ratios, it was to be expected that the lots of colloidal material successively isolated from the Sassafras and Huntington subsoils would vary from each other more than the successive samples isolated from the Sharkey and Vega Baja soils.

The procedure adopted for extracting the colloidal material was somewhat different from that described on page 8, although the colloidal material was graded from the larger particles in the same manner, by use of the supercentrifuge, and concentrated similarly by use of Chamberland-Pasteur filters. The method of dispersing the colloidal material was so much more effective than the method first used that large samples of soil were undesirable. The separations described below were made with samples varying from 25 pounds of the Marshall soil to 1 pound of the Vega Baja soil.[9]

The colloidal material was dispersed by gently rubbing the soil when in a pasty condition with a rubber pestle, or, in the case of large samples, by kneading with the hands. From 5 to 20 times as much water as soil was added, and after thorough agitation the resulting suspension was allowed to settle overnight before decanting. One part of ammonium hydroxide in 3,000 parts of distilled water was used for promoting deflocculation.

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[9] As the work progressed the samples were reduced from 25 pounds to about 2 pounds, since it was found possible to eliminate losses of the finer soil material when the suspensions were passed through the supercentrifuge. In working with the Sassafras subsoil and the Marshall soil considerable suspended matter escaped through the bottom of the centrifuge bowl and became contaminated with oil on the bearing, so that it had to be discarded. These losses were avoided when working with the other three soils. By using water in place of oil for lubrication it was possible to recover and rework the material escaping from the centrifuge bowl. In the case of the Huntington subsoil a slight amount of material was lost, but in the case of the Sharkey and Vega Baja soils extraction and recovery of the colloidal material was practically quantitative; hence the results show the total quantities of this class of material present in these soils.

The residue left after decantation of the suspended material was repeatedly treated in the same manner as the original soil until it was apparent that no more material was to be dispersed by these means. This residue contained all the larger soil particles and constituted the "coarse fraction" discussed later. The decanted suspensions were run through the supercentrifuge and the colloidal material passing through was concentrated as previously described on pages 8 and 9. The material remaining in the bowl of the supercentrifuge was recovered and kept separate from the fraction of coarser soil particles. It was repeatedly rubbed and treated with water in the same way as the coarser material until it was apparent that no more material capable of passing the supercentrifuge was to be obtained. The residue left, called "fine" fraction or residue, contained chiefly particles of 1 to 50 microns diameter, although the material was not rigidly graded. By keeping the coarser and finer particles separate in this way, isolation of the colloidal material was facilitated considerably. It should be borne in mind that the fine and coarse fractions do not represent definite classes of soil material as the colloid fraction does. After the finer residues had become pretty well exhausted of extractable material, boiling the residues for 6 to 12 hours was resorted to in some cases. This treatment, however, did not seem to increase the quantity of colloid obtainable, although it probably did reduce slightly the number of treatments required. The fine and coarse residues were rubbed and treated with water 24 to 81 times to disperse all the colloidal material, and the total amount of water used for the completed separation varied between 200 and 2,000 times the weight of the soil sample.

The chief object in making this separation was to see whether the colloidal material brought into suspension by successive treatments of the same soil differed essentially in its adsorptive capacity. Hence in most cases the first fraction of colloidal matter collected was composed of the first four treatments of washings of the soil. This was comparable with the material isolated for determining the adsorption ratios given in Table 2. The second, or second and third, fractions of colloidal material were obtained from a large number of succeeding washings of the soil and usually represented the greater part of the colloid material extractable by the means employed. The last fraction of colloidal material, except in the case of the Huntington subsoil, was composed of material which yielded to dispersion less readily than the preceding fractions. The suspensions from which the last fraction was obtained were noticeably less concentrated than those obtained from the preceding washings of the soil. The last or fourth fraction of the Huntington subsoil was different from any of the other fractions extracted for this particular study. It was composed of material which had remained for several days in suspension, but which had nevertheless been thrown out by the supercentrifuge. It contained practically no particles larger than 1 micron in diameter, coarser particles having been removed by subsidence.

The quantities of colloidal material constituting each successive fraction isolated are given in Table 3. In column 2 the quantities are expressed as percentage of the whole soil and in column 6 as percentage of all the colloidal material isolated. The adsorptive capacity of each fraction of colloidal material for dye, water, and ammonia is given in columns 3 to 5, and in columns 7 to 9 the relative adsorptive capacities of the different fractions are given, the adsorptive capacity of the first fraction extracted being expressed as 100 in each case.

TABLE 3.—*Adsorptive capacities of colloidal materials successively extracted from the same soil.*

Colloidal material.	Quantity of colloidal material extracted, in percentage of whole soil.	Adsorption per gram of colloidal material.			Quantity of colloidal material in percentage of all colloidal material isolated.	Relative adsorptive capacities of different fractions of colloidal material for—		
		Dye.	H_2O.	NH_3.		Dye.	H_2O.	NH_3.
Huntington loam, subsoil:	*Per ct.*	*Gram.*	*Gram.*	*Gram.*	*Per ct.*			
First fraction of colloid	2.10	0.1437	0.2998	0.0324	19.8	100	100	100
Second fraction of colloid	6.06	.1174	.2679	.0301	57.1	82	89	93
Third fraction of colloid	2.12	.0998	.2049	.0235	20.0	69	68	73
Fourth fraction of colloid	.33	.0477	.1194	.0144	3.1	33	40	44
Total quantity colloid extracted	10.61	.1169	.2570	.0287	100	81	86	89
Marshall silt loam, soil:								
First fraction of colloid	.64	.3159	.3090	.0611	9.1	100	100	100
Second fraction of colloid	4.50	.3035	.2951	.0579	64.2	96	96	95
Third fraction of colloid	.97	.2906	.2902	.0598	13.8	92	94	98
Fourth fraction of colloid	.90	.1916	.2328	.0553	12.8	61	75	91
Total quantity colloid extracted	7.01	.2885	.2877	.0581	100	91	93	95
Sassafras silt loam, subsoil:								
First fraction of colloid	.88	.2058	.3388	.0387	14.2	100	100	100
Second fraction of colloid	3.05	.1778	.3053	.0406	49.3	86	90	105
Third fraction of colloid	1.76	.2079	.3006	.0412	28.4	101	89	106
Fourth fraction of colloid	.50	.2121	.2719	.0388	8.1	103	80	100
Total quantity colloid extracted	6.19	.1931	.3060	.0404	100	94	90	104
Sharkey clay, soil:								
First fraction of colloid	12.1	.4044	.3237	.0609	31.4	100	100	100
Second fraction of colloid	11.9	.3995	.3271	.0572	30.9	99	101	94
Third fraction of colloid	12.3	.5043	.2646	.0460	32.0	125	82	76
Fourth fraction of colloid	2.2	.3576	.3211	.0553	5.7	88	99	91
Total quantity colloid extracted	38.5	.4321	.3057	.0547	100	107	94	90
Vega Baja clay loam, soil:								
First fraction of colloid	16.6	.0584	.3125	.0206	54.6	100	100	100
Second fraction of colloid	12.7	.0463	.2749	.0165	41.7	79	88	80
Third fraction of colloid	1.1	.0494	.3298	.0182	3.6	85	106	88
Total quantity colloid extracted	30.4	.0530	.2974	.0188	100	91	95	91

On the whole, the different colloidal fractions isolated from the same soil were very similar in adsorptive capacity to the first sample extracted. In only two or three cases did any of the fractions differ from the first fraction by more than 25 per cent. In the case of the Marshall soil and the Huntington subsoil there was a gradual decrease in the adsorptive capacities of the lots of colloid successively extracted; but this does not hold for the other three soils. Chemical analyses made of the different colloidal fractions also showed that there was no marked variation between the first two or three fractions in ultimate chemical composition. The content of iron, aluminum, and silica was very constant in all fractions except the last; this in some cases was higher in silica and lower in iron and alumina than the preceding fractions. The chemical composition is discussed in detail in an unpublished report (Robinson and Holmes, *27*).

So far as the adsorption method of determining the colloidal material in soils is concerned, the important comparison is between the adsorptive capacity of the first fraction of colloid and that of the total quantity extracted. It will be noted that all the fractions of colloid taken together ("total quantity colloid extracted") had practically the same adsorptive capacity as the first fraction. The differences are less than 10 per cent. except in the case of the Huntington subsoil. It is significant in connection with the cause of the disagreement between the dye, water, and ammonia ratios given in Table 2, that the slight variations between the adsorptive capacities of the first fraction and the combined fractions were practically the same for malachite green as for water or ammonia.

Although this comparison of the samples of colloid successively extracted from a soil was not undertaken with a view to determining quantitatively the total amount of colloidal material that it was possible to isolate by the procedure outlined, nevertheless the total quantity of colloidal material recovered is a matter of considerable interest. It will be noted that the quantity of colloidal material actually extracted from the different soils was 6.19 to 38.5 per cent of the weight of the whole soil. This is highly important in bearing on the opinion held by Schloesing 40 years ago, and still widely current, that soils contain less than 2 per cent of truly colloidal material. It is improbable that Schloesing was dealing with a product in a finer state of dispersion than that obtained in this separation inasmuch as he was obliged to rely on time of subsidence for grading his material. As mentioned on page 9, suspensions passing through the supercentrifuge in this work apparently contained very few particles larger than 0.3 micron in diameter.

The quantities of colloidal material separated from the Sassafras subsoil and Marshall soil were doubtless considerably less than the quantities of this class of material actually present in the soil. As already pointed out, considerable losses of the fine material of these soils occurred in preparing the samples of colloidal material. In the cases of the Huntington subsoil, the Sharkey soil, and the Vega Baja soil the quantities of supercentrifuge colloid isolated represent practically all this class of material that it was possible to separate by the means employed.

To return to the question of the sample of colloidal material as a factor affecting the accuracy of colloid determinations by the adsorption method, it appears that so far as adsorptive capacity is concerned a small sample of extractable colloidal material differs by approximately 10 per cent from all the colloidal material which is isolatable by the methods described above. Of course the colloid which it was impossible to extract with the methods employed might have a different adsorptive capacity for dye, water, or ammonia than the colloid which was extracted. However, to account for the disagreement in the ratios on the basis of an unfair sample of the colloid the degree of difference between the adsorptive capacities of the extractable and unextractable colloidal material would have to be different with respect to dye, water, and ammonia. Evidence on this point is given in the following section.

Comparison of the extractable and unextractable colloidal material.— The adsorptive capacities of the extracted and the unextracted colloidal material can not be directly compared, but an indirect comparison of the two kinds of colloid is possible. If the extractable colloidal material is completely separated from the soil as in the work just described, the unextracted colloidal material will all be present in the residual fractions of fine and coarse material, mixed, of course, with the mineral fragments above colloidal size.

A comparison, then, of the adsorptive capacity of the fine or coarse fraction for dye, water, and ammonia with the adsorptive capacity of the extracted colloidal material for these three substances will show whether the unextracted colloid differs from the extracted colloid more in its adsorption of dye than in its adsorption of water or ammonia. This comparison would show only the relation between the dye, water, and ammonia adsorptive capacities of the extracted and unextracted colloids. It would not show, for example, whether the unextracted colloid was 80 per cent or 40 per cent as adsorptive for all three substances as the extracted colloid. However, the adsorption ratios of the fine and coarse fractions,

$$\frac{\text{adsorption per gram of fraction}}{\text{adsorption per gram of extracted colloid}}$$

will, other things being equal, show the absolute quantities of colloid in the fractions in proportion as the adsorptive capacities of the extracted and unextracted colloids are alike. Now it is possible to determine the quantities of colloid in the fine and coarse fractions by microscopical observation with considerable accuracy (Fry, *13*). Hence a comparison of the quantities of colloid found by microscopical observation with the quantities indicated by the adsorption ratios will show approximately the relative adsorptive capacities of the extracted and unextracted colloidal materials. If the adsorption ratio shows a smaller percentage of colloidal material than the microscopical determination, it indicates that the unextracted colloidal material has a lower adsorptive capacity than the sample of extracted colloid and vice versa.

The soil fractions prepared in order to compare the successive fractions of extractable colloidal material were not well suited for a comparison of the extractable and unextractable colloid since considerable portions of the fine and coarse fractions were lost, except in the case of the Vega Baja soil. Accordingly new fractionations of soils were made, taking care to avoid losses of colloidal, fine, or coarse material.

The methods of extracting and concentrating the colloidal material and of separating the fine and coarse residues were essentially the same as those described on pages 16 to 17. The important difference was that in this work a bottle centrifuge was used for separating the colloidal material from the noncolloidal particles instead of the supercentrifuge, the speed and time of centrifuging being so regulated as to leave in suspension all particles less than 1 micron in diameter. The centrifuge used had a diameter of 22 inches. When running at a speed of 850 revolutions per minute about 45 minutes were usually required for throwing out particles larger than 1 micron in diameter. This was checked by microscopic observation of the colloidal, fine, and coarse fractions. The colloidal material passing through the supercentrifuge in the extractions described on pages 16 and 17 contained, as near as could be judged by observation, very few particles larger than 0.3 micron. Hence the difference between the colloidal material obtained in previous extractions and that obtained in this separation consisted in the fact that in the first case the upper limit of size of particles was in the neighborhood of 0.3 micron while in the latter case the upper limit of size was 1 micron.

The finer and coarser soil particles above colloidal size were collected in separate fractions as in the previous separation, but in this separation a quantitative recovery of these fractions was attempted. The samples of soil fractionated in this way consisted of 50 grams of Sharkey soil and 100 grams each of Cecil soil, Huntington soil, Huntington subsoil and Sassafras subsoil.

Table 4 shows the quantities of colloidal, fine and coarse materials separated from each soil, together with the adsorptive capacities of these materials and of the unfractionated soils. Included in this table, also, are the results obtained with two samples of soil—the Vega Baja soil and a second sample of Sharkey soil—which were fractionated according to the method described on pages 16 to 17; that is, the colloidal material was graded by the supercentrifuge, so the upper limit of the particles was about 0.3 micron instead of 1 micron.[10]

TABLE 4.—*Adsorptive capacities of soils and soil fractions.*

Description of soil fractions.	Part of whole soil.	Adsorption per gram of material.		
		Dye.	H_2O.	NH_3.
	Per cent.	*Gram.*	*Gram.*	*Gram.*
Cecil clay loam, soil:				
Whole soil	100.0	0.0078	0.0442	0.0034
Colloid	9.4	.0840	.2439	.0165
Fine fraction	7.6	.0154	.0714	.0076
Coarse fraction	83.8	.0000	.0028	.0010
Cecil clay loam, soil (duplicate determination):				
Whole soil	100.0	.0078	.0442	....
Colloid	9.4	.0975	.2834	....
Fine fraction	10.4	.0007	.0509	....
Coarse fraction	78.3	.0000	.0042	....
Huntington loam, soil:				
Whole soil	100.0	.0245	.0533	.0104
Colloid	10.3	.0949	.2221	.0270
Fine fraction	21.9	.0288	.0476	.0098
Coarse fraction	64.0	.0114	.0215	.0062
Huntington loam, subsoil:				
Whole soil	100.0	.0182	.0792	.0083
Colloid	13.3	.0918	.2996	.0226
Fine fraction	19.4	.0143	.0665	.0072
Coarse fraction	63.3	.0053	.0292	.0031
Sassafras silt loam, subsoil:				
Whole soil	100.0	.0276	.0568	.0074
Colloid	14.4	.1398	.2732	.0293
Fine fraction	20.6	.0222	.0546	.0079
Coarse fraction	61.9	.0053	.0041	.0004
Sharkey clay, soil:				
Whole soil	100.0	.1997	.1755	.0345
Colloid	42.4	.3790	.2956	.0520
Fine fraction	53.1	.0657	.0772	.0172
Sharkey clay, soil (separation by supercentrifuge):				
Whole soil	100.0	.2128	.1984	.0358
Colloid	31.5	.3592	.3037	.0514
Fine fraction	38.9	.1075	.1280	.0244
Coarse fraction	31.8	.0825	.0834	.0168
Vega Baja clay loam, soil (separation by supercentrifuge):				
Whole soil	100.0	.0369	.1805	.0147
Colloid	30.5	.0530	.2974	.0187
Fine fraction	38.6	.0492	.2332	.0196
Coarse fraction	31.8	.0094	.0260	.0044

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[10] In the case of the Sharkey soil absolutely all the extractable colloidal material was not isolated, since the fractionation was undertaken chiefly for the study, to be described later, on the "alteration in adsorptive capacity of the colloid produced by extraction."

In the case of all soils, except the Sharkey (separation by supercentrifuge), the quantities of colloid isolated were all that could be obtained with the methods employed. The coarse and fine fractions of all soils except this one, therefore, contain only what we may term "unextractable" colloid.[11] The fine and coarse fractions of the Sharkey soil (separation by supercentrifuge) on the other hand contain a small amount of colloid capable of isolation in addition to the unextractable.

The quantity of colloidal material present in these fine and coarse fractions was estimated with the petrographic microscope. The details and accuracy of the method have been described by Fry in another publication (*13*).

Microscopical determinations of the colloidal material present in the fine and coarse fractions of Table 4 are reported in Table 5. Table 5 also shows the quantities of colloidal material in the fine and coarse fractions which the dye, water, and ammonia adsorption ratios

$$\frac{\text{adsorption per gram of fraction}}{\text{adsorption per gram of extracted colloid}}$$

indicate. The adsorption ratios were calculated from data given in Table 4.

TABLE 5.—*Percentages of unextracted colloid in fine and coarse soil fractions.*

Description of samples.	Percentage of colloidal material in the sample indicated by—			
	Microscopical count.	Dye adsorption ratio.	Water adsorption ratio.	Ammonia adsorption ratio.
Cecil clay loam, soil:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Fine fraction	74	18.3	29.3	46.1
Coarse fraction	4	.0	1.1	6.1
Cecil clay loam, soil (duplicate determination):				
Fine fraction	55	.7	18.0	....
Coarse fraction	4	.0	1.5	....
Huntington loam, soil:				
Fine fraction	48	30.3	21.4	36.3
Coarse fraction	8	12.0	9.7	23.0
Huntington loam, subsoil:				
Fine fraction	25	15.6	22.2	31.9
Coarse fraction	10	5.8	9.7	13.7
Sassafras silt loam, subsoil:				
Fine fraction	38	15.9	20.0	26.9
Coarse fraction	2	3.8	1.5	1.4
Sharkey clay, soil:				
Fine fraction	42	17.3	28.1	33.1
Sharkey clay, soil (separation by supercentrifuge):				
Fine fraction	52	29.9	42.1	47.5
Coarse fraction	25	23.0	27.5	32.7
Vega Baja clay loam, soil (separation by supercentrifuge):				
Fine fraction	97	92.8	78.4	104.3
Coarse fraction	14	17.7	8.7	23.4

Both microscopical determinations and adsorption ratios indicate that a considerable quantity of colloidal material is left in the fractions of finer soil residues in spite of the repeated washing and rubbing to which this material was subjected. In the coarser soil residues, however, very little colloidal material is present as a rule. One would expect this colloidal material to differ in adsorptive capacity from the material which was isolated, from the mere fact that it was not brought into suspension by the same treatment.

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[11] It may well be that there is no real distinction between the colloid which was extracted and that which was not.

As already pointed out, evidence as to whether the unextracted colloid differs in adsorptive capacity from the extracted colloid can be obtained by comparing the quantities of colloid determined microscopically with the quantities indicated by the adsorption ratios. If the adsorption ratios indicate the same percentages of colloidal material as the microscopical observations the colloid in the residues presumably has the same adsorptive capacity as the extracted colloid. If the adsorption ratios are lower than the microscopical determinations, it is to be assumed that the unextracted colloid in the fractions has a lower adsorptive capacity per gram than the colloid extracted, and if the adsorption ratio is higher than the microscopical determination the unextracted colloid doubtless is more adsorptive than the extracted colloid.

Comparisons of the microscopical and adsorption determinations given in Table 5 indicate that the unextracted colloidal material usually has a considerably lower adsorptive capacity for dye and water than the extracted colloid, but the adsorptive capacities of the two kinds of colloid for ammonia is as a rule approximately alike.

It should be borne in mind that these estimations of the relative adsorptive capacities of the extractable and unextractable colloids apply on the one hand to material in the condition in which it is after extraction and on the other hand to material in the unextracted condition. If it is true that the process of extraction does not alter the adsorptive capacity of either the extracted or unextracted colloid, it would follow that the two kinds of colloidal material—if they are distinct kinds—have different adsorptive capacities as they exist in the untreated soil. However, data presented in the following pages indicate that the colloidal material after extraction probably has a somewhat different adsorptive capacity from what it had in the untreated soil. In Table 9 the adsorptive capacities of the extractable colloid before and after extraction are given, and the probable relation between the adsorptive capacities of the colloid in the two conditions is expressed in factors given in columns 8 to 10 of that table.

For a comparison, then, of the adsorptive capacities of extractable and unextractable colloids as they exist in the untreated soil, it is necessary to correct the adsorption ratios given in Table 5 for possible alteration produced in the extracted colloid, upon which the ratios are based. Factors given in Table 9 were used for this purpose. The corrected adsorption ratios and microscopical determinations on samples containing an appreciable amount of colloidal material are given in Table 6.[12]

Data in Table 6 show that even in the untreated soil the extractable and unextractable colloids usually differ considerably in adsorptive capacities. The difference in adsorptive capacities of the two kinds of colloid is not at all constant; it is large in the case of the Cecil soil and practically negligible in the case of the Vega Baja soil. In most cases the unextractable colloid is more nearly equal to the extractable colloid in adsorptive capacity for ammonia than in adsorptive capacity for water or dye. This is apparent also on averaging the results of the ten samples. The adsorptive capacity of the unextracted colloid averages 64 per cent that of the extracted colloid for dye, 58 per cent for water and 83 per cent for ammonia.

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[12] Samples containing a small quantity of colloidal material had such low adsorptive capacities that the adsorption ratios could not be determined accurately. The comparisons of the adsorption ratios and microscopical determinations of colloid were, therefore, not significant in the case of these samples (Table 5), and they were omitted from Table 6.

TABLE 6.—*Relative adsorptive capacities of extractable and unextractable colloidal material, as indicated by the relative percentages of colloid shown by microscopical and by corrected adsorption ratio determinations.*

Soil fraction in which colloid present.	Colloid present by microscopical count.	Colloid present by corrected—			Adsorptive capacity of unextractable colloid for dye, H_2O, and NH_3, expressed relative to adsorptive capacity of the extractable colloid taken as 100 in each case.		
		Dye adsorption ratio.	Water adsorption ratio.	Ammonia adsorption ratio.	Dye.	H_2O.	NH_3.
Cecil clay loam soil:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*			
Fine fraction	74	22	18	36	28	23	49
Fine fraction (duplicate)	55	1	14	....	2	25	....
Huntington loam:							
Soil, fine fraction	48	30	18	26	63	38	54
Subsoil, fine fraction	25	17	20	21	68	80	84
Sassafras silt loam:							
Subsoil, fine fraction	38	17	19	22	45	50	58
Sharkey clay soil:							
Fine fraction	42	18	26	31	43	62	71
Separation by supercentrifuge—							
Fine fraction	52	23	32	35	44	62	67
Coarse fraction	25	17	21	24	68	84	96
Vega Baja clay loam, soil (separation by supercentrifuge):							
Fine fraction	97	98	85	101	101	88	104
Coarse fraction	14	19	9	23	136	64	164

Conclusions regarding representativeness of a sample of colloidal material.—The data obtained on the adsorptive capacities of successive lots of colloidal material isolated from the same soil and on the relative adsorptive capacities of the extractable and unextractable colloid show that a small sample of colloidal material is not exactly representative of all the colloid present in many soils. Part, therefore, of the disagreements between the quantities of colloid indicated by the dye, water, and ammonia adsorption ratios in Table 2, may be ascribed to failure to obtain an exactly representative sample of the colloidal material. Sampling of the colloidal material, however, does not appear to be the only cause of disagreement in the adsorption ratios.

A small sample of the extractable colloidal material which is dispersable into particles less than 0.3 micron in size appears to be about 90 per cent representative of all this class of material. The chief error in sampling appears to be due to the unextractable collodial material in many, but not all, soils having a different adsorptive capacity from that of the extractable colloidal material. A small sample of the colloidal material seems to represent more nearly all the colloidal material in its adsorptive capacity for ammonia than in its adsorptive capacity for water or dye.

The difference in the adsorptive capacities of the extracted and unextracted colloids may of course be due to a difference in the chemical composition of the two kinds of colloids or due merely to a difference in the physical state, as fineness of subdivision or degree of induration of the colloidal material. Certain indications point to the latter possibility. Pressure alone, however, does not appear to alter the adsorptive capacity of the air-dried colloid. Dr. L. H. Adams, of the Geophysical Laboratory of the Carnegie Institution, very kindly subjected a sample of air-dried Sharkey colloid to pressures up to 15,000 atmospheres. The colloidal material, which contained 11 per cent of moisture when under pressure, was not changed in adsorptive capacity. This is evident from the results given in Table 7.

TABLE 7.—*Effect of pressure on adsorptive capacity of the Sharkey soil colloid.*

Treatment of sample.	H_2O adsorbed per gram of material.	Dye adsorbed per gram of material.
	Gram.	*Gram.*
Not compressed	0.3103	0.4365
Exposed to 4,000 atmospheres pressure	.3082	.4395
Exposed to 7,000 atmospheres pressure	.3078	.4395
Exposed to 15,000 atmospheres pressure	.2932	.4220

ALTERATION IN ADSORPTIVE CAPACITY OF THE COLLOID PRODUCED BY EXTRACTION.

From data presented in Table 4, evidence can be obtained as to whether the adsorptive capacity of the colloidal material is affected by extraction. Table 4 gives the adsorptive capacity of the untreated soil and the adsorptive capacities, as well as percentages, of the colloidal material and other fractions into which the soil was separated. If isolation of the colloidal material does not affect the adsorptive capacity of the colloidal material, the adsorptions of the separates into which the soil is divided (colloidal material, fine and coarse fractions) should amount to just what the untreated soil adsorbs. If, on the other hand, the quantity of dye, water, or ammonia adsorbed by the combined colloidal, fine and coarse fractions amounts to more or less than the quantity of these substances adsorbed by the untreated soil, it is apparent that the adsorptive capacities of the colloidal material must be altered by the process of fractionation.

Table 8 gives the quantities of dye, water, and ammonia adsorbed by one gram of the untreated soil and the quantities of these substances that would be adsorbed by 1 gram of the soil separates combined according to the percentages of each isolated from the soil. It is apparent from the data in Table 4 that the quantities of colloidal material, fine and coarse fractions isolated from a soil, do not exactly equal the amount of soil taken for fractionation, the quantities of separates recovered ranging from 95.5 per cent to 102.2 per cent of the original samples. The losses of soil material were probably chiefly mechanical, although with the large volumes of water used there must have been some losses occasioned by solubility. A certain amount of contamination was also more or less inevitable in treating 50 to 100 grams of soil with 100 to 200 liters of water, without special refinement in equipment. For the purposes of the comparison in Table 8 it was assumed that the slight loss or gain of soil material applied to the soil as a whole, i. e., it was distributed among the soil separates in the proportions the separates were present in the soil. In calculating for Table 8 the quantities of dye, water, and ammonia that would be adsorbed by 1 gram of the combined soil separates a correction was applied on this assumption regarding the gain or loss in material during fractionation.[13]

TABLE 8.—*Adsorption by the untreated soil and by the combined soil separates.*

Description of material.	Adsorption per gram of material.			Amount adsorbed by combined soil separates relative to amount adsorbed by untreated soil taken as 100.		
	Dye.	H_2O.	NH_3.	Dye.	H_2O.	NH_3.
Cecil clay loam, soil:	*Gram.*	*Gram.*	*Gram.*			
Untreated soil	0.0078	0.0442	0.0034	100	100	100
Combined soil separates	.0090	.0305	.0029	115	69	85
Cecil clay loam, soil (duplicate determination):						
Untreated soil	.0078	.0442	....	100	100	....
Combined soil separates	.0094	.0359	....	121	81	....
Huntington loam, soil:						
Untreated soil	.0245	.0533	.0104	100	100	100
Combined soil separates	.0243	.0487	.0092	99	92	88
Huntington loam, subsoil:						
Untreated soil	.0182	.0792	.0083	100	100	100
Combined soil separates	.0191	.0742	.0066	105	94	80
Sassafras silt loam, subsoil:						
Untreated soil	.0276	.0568	.0074	100	100	100
Combined soil separates	.0289	.0551	.0063	104	96	85
Sharkey clay soil:						
Untreated soil	.1997	.1755	.0345	100	100	100
Combined soil separates	.2048	.1742	.0327	103	99	95
Sharkey clay, soil (separation by supercentrifuge):						
Untreated soil	.2128	.1984	.0358	100	100	100
Combined soil separates	.1773	.1683	.0303	83	85	85
Vega Baja clay loam, soil (separation by supercentrifuge):						
Untreated soil	.0369	.1805	.0147	100	100	100
Combined soil separates	.0378	.1873	.0146	102	104	99

In most cases the quantities of dye, water, and ammonia adsorbed by the combined separates appear to agree with the quantities of these substances adsorbed by the untreated soil as closely as could be expected, considering the accuracy of the adsorption methods employed. However, the relative figures for the adsorptions by the untreated soils and the combined separates disclose what seems to be a significant fact. The adsorption of dye by the combined separates in almost every case is slightly higher than that of the untreated soil, while the adsorption of ammonia by the combined separates in every case is slightly or considerably less than that of the untreated soil. Adsorption of water by the combined separates in 7 of 8 cases is slightly less than that of the untreated soil.

If these results are significant and not due to experimental error, they show that the procedure of separation has rendered the colloidal material slightly more adsorptive of dye, slightly less adsorptive of water, as a rule and considerably less adsorptive of ammonia than the colloidal material as it exists in the untreated soil. If the colloid after extraction adsorbs more than it does in the soil, this would, of course, make the ratio

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[13] For example: The Huntington soil separates totaled 96.2 per cent of the whole soil (see Table 4). The dye adsorption of 1 gram of the combined separates was thus taken as being the sum of 0.103×0.0949, 0.219×0.0288, and 0.64×0.0114, divided by 0.962.

$$\frac{\text{adsorption per gram soil}}{\text{adsorption per gram colloid}}$$

too low and vice versa. Such an alteration in the adsorptive capacity of the colloidal material for the different substances would explain the fact brought out in Table 2; namely that in most cases where there is a marked disagreement in the quantities of colloid indicated by the dye, water, and ammonia adsorption ratios the dye ratio is the lowest and the ammonia ratio is the highest.

Although the differences between the adsorptions of the untreated soil and the combined soil separates are small, and in most cases about what should be allowed for experimental error, the constancy with which the combined separates exceed the untreated soil in dye adsorption and fall short of the untreated soil in ammonia adsorption [14] indicate that we have to do with a real effect. Also, the greatest variations occur in the adsorption of ammonia and this determination is probably slightly more accurate than the determination of dye or water adsorbed.

However, even if the values given in Table 8 were absolutely accurate, they probably would not indicate the exact degree of alterations of the colloids in the process of extraction. The data given in Table 8 are calculated on the assumption that all the adsorptive, or colloidal, matter has been altered in the process of extraction. As a matter of fact, if there is an alteration in adsorptive capacity, it probably takes place chiefly or only in the colloid which is extracted. The unextracted colloid in the fine and coarse fractions is doubtless in essentially the same condition it was in the untreated soil. The extracted colloid, however, has been converted from the gel to the sol condition and this increased dispersion, or a change in the material incident to the increased dispersion, is possibly responsible for the change in adsorptive capacity.

Table 9 shows the alteration in adsorptive capacity of the extracted colloid, calculated on the assumption that only the extracted colloid is changed in the process of extraction. Data used as the basis for this calculation are given in Table 4. The quantity of dye, water, or ammonia adsorbed by the amount of fine and coarse residues fractionated from 1 gram of soil is subtracted from the quantity of dye, water, or ammonia adsorbed by 1 gram of the untreated soil. The difference between the two adsorptions—that of the whole soil, and that of the combined fine and coarse fractions—must represent the amount adsorbed in the extractable colloid as it existed in the untreated soil. This calculated adsorption of the extracted colloid as in the soil, is compared with the determined adsorption of the colloid as extracted, both adsorptive capacities being expressed on the per gram basis. Just as in the previous calculation, it is assumed in these calculations that the slight losses, or gains, in material taking place during fractionation were from the soil as a whole, and the adsorptions of the untreated soil given in Table 4 were decreased or increased from the observed values to allow for these losses or gains.

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[14] If alteration in the adsorptive capacity of the colloid produced by extraction is a cause of the disagreement between dye, water, and ammonia ratios, one would not expect to find marked differences in alteration for dye and ammonia in the case of the Sharkey and Vega Baja soils, since the dye, water, and ammonia ratios on these soils agreed well. As a matter of fact there is noticeably less difference between the degree of alteration for dye and ammonia in the case of these soils than in the case of the others.

TABLE 9.—*Influence of extraction on the adsorptive capacity of the colloidal material.*

Soil from which colloid obtained.	Gram of dye adsorbed per gram of extractable colloidal material.		Gram of H_2O adsorbed per gram of extractable colloidal material.		Gram of NH_3 adsorbed per gram of extractable colloidal material.		Adsorption by colloid when extracted divided by adsorption by colloid when in soil.		
	When colloid in soil.	When colloid extracted.	When colloid in soil.	When colloid extracted.	When colloid in soil.	When colloid extracted.	Dye.	H_2O.	NH_3.
Cecil clay loam, soil	0.0712	0.0840	0.3913	0.2439	0.0214	0.0165	1.18	0.62	0.77
Cecil clay loam, soil (duplicate determination)	.0806	.0975	.3700	.2834	....	....	1.21	.77	....
Huntington loam, soil	.0961	.0949	.2621	.2221	.0379	.0270	.99	.85	.71
Huntington loam, subsoil	.0850	.0918	.3353	.2996	.0346	.0226	1.08	.89	.65
Sassafras silt loam, subsoil	.1306	.1398	.2868	.2732	.0368	.0293	1.07	.95	.80
Sharkey clay, soil	.3675	.3790	.2986	.2956	.0561	.0516	1.03	.99	.92
Sharkey clay, soil (separation by supercentrifuge)	.4744	.3592	.4014	.3037	.0691	.0514	.76	.76	.74
Vega Baja clay loam, soil (separation by supercentrifuge)	.0501	.0530	.2749	.2989	.0193	.0188	1.06	1.09	.97

The numbers in columns 8 to 10 show the extent to which the adsorptive capacity of the extractable colloid has probably been altered by the process of extracting it from the soil. These alterations, calculated on the assumption that the unextracted colloidal material is unaffected by the extraction process, are somewhat greater than the values given in Table 8, columns 5 to 7, which were calculated on the assumption that the unextracted material was altered as well as the extracted. The same general conclusions, however, are to be drawn from these calculations as from those given in the previous table. In practically all cases the process of extraction appears to have rendered the colloidal material slightly more adsorptive of dye, slightly less adsorptive of water, and considerably less adsorptive of ammonia.

It is conceivable that apparently unimportant variations in the process of extracting the colloidal material, such as in the volume of water used, might affect the adsorptive capacity of the extracted colloid. However, this should not affect the calculated values for the adsorptive capacity of the colloid when in the soil. As a matter of fact, the calculated values for the adsorptive capacity of colloid "when in the soil" show a fair agreement in the case of the two samples of Cecil soil. In the case of the two samples of Sharkey soil the calculated values for the adsorptive capacities of the colloids when in the soil should not agree, since the two colloids are different. The colloidal material of the first sample of Sharkey soil given in the table contains particles up to 1 micron in diameter and the colloidal material of the second sample contains only particles that would pass through the supercentrifuge, i. e., particles up to probably 0.3 micron in diameter. As might be expected, the second sample with the smaller particles shows the higher adsorptive capacity.

Although no great accuracy can be claimed for the "alteration values" given in columns 8 to 10, it is believed, that they measure approximately a real effect. The alteration values explain to a considerable extent why the amounts of colloid in certain soils calculated from the dye, water, and ammonia adsorption ratios

$$\frac{\text{adsorption per gram of soil}}{\text{adsorption per gram of colloid}}$$

do not agree. It will be seen from the data to be given in Table 10 that when the adsorption ratios are corrected for the differences in the adsorptive capacity of the colloid "as extracted" and "as in the soil," the dye, water, and ammonia determinations show a reasonable agreement.

The chief source of inaccuracy in the calculated values given in Tables 8 and 9 is probably the uncertainty regarding the slight losses or gains of soil material occurring during separation of the colloid. If the loss of soil material were preponderantly colloid instead of the soil as a whole, the values calculated for the adsorptive capacity of the colloid when in the soil would be somewhat lower than those given in Table 9 and the amount adsorbed by the combined soil separates would be somewhat higher than the values given in Table 8. The relation between the dye, water, and ammonia values would, however, be little affected. For example, if in the case of the Huntington soil the 3.8 per cent loss of material were all colloid, it would appear that the colloid when extracted was 1.25 as adsorptive for dye, 1.08 as adsorptive for water and 0.89 as adsorptive for ammonia as the colloid when in the untreated soil. It will be noted that the relation between these values is virtually the same as between the respective values 0.99, 0.85, and 0.71 given in Table 9, calculated on the assumption that the 3.8 per cent loss was from the soil as a whole. Hence, so far as bringing about agreement in the adsorption ratios is concerned, it would make little difference which set of alteration values was used, although it would make a difference in the percentage of colloid shown by the ratio to be present in the soil.

The subject of alteration in the adsorptive capacity of the colloidal material on extraction should be investigated further. With a refinement of methods it should be possible to determine with greater accuracy the difference in adsorptive capacity of the colloidal material as it is in the soil and as it is extracted, if such a difference exists. Little evidence is at hand to show whether such an alteration would be produced by the mere increased dispersion of the colloidal particles, by the leaching of soluble salts, or by the manner of concentrating and drying the colloidal material.

ACCURACY OF THE ADSORPTION METHOD.

The data given in pages 14 to 29 indicate that the method of determining the percentage of colloid in the soil from the adsorption ratio,

$$\frac{\text{adsorption per gram of soil}}{\text{adsorption per gram of colloid}}$$

may be somewhat inaccurate owing to two causes—inability to obtain a fair sample of all the colloidal material in the soil and alteration in adsorptive capacity of the colloidal material produced by extraction. Each of these sources of error affects the dye, water, and ammonia determinations oppositely or to slightly different extents.

The error caused by inability to secure a sample of colloidal material which is exactly representative of all in the soil apparently is not large in the case of most soils. Data given in Table 3 indicate that a small sample of colloidal material is usually only 5 to 10 per cent more adsorptive for dye, water, or ammonia than all the colloidal material which is extractable by our methods. However, a small or large sample of the extractable colloid as a rule does not appear to be closely representative in adsorptive capacity of the unextractable colloid. Data given in Table 6 indicate that the unextractable colloid in one soil was only one-fourth as adsorptive as the extracted colloid for one substance. In other soils examined, however, the unextracted colloid was 60 to 100 per cent as adsorptive for all three substances—dye, water, and ammonia—as the extracted material. Errors induced by the different adsorptive capacities of the extractable and unextractable colloids are reduced by the fact that the unextractable colloid usually constitutes only about one-half of the total colloidal material (Fry, *13*). The unextracted colloid as a rule is more nearly like the extracted colloid in its adsorptive capacity for ammonia than in its adsorptive capacity for dye or water. The error in sampling the colloidal material would, therefore, make the ratio

$$\frac{\text{adsorption per gram of soil}}{\text{adsorption per gram of colloid}}$$

too low, but the ammonia ratio should, on the whole, be least affected by this error.

The alteration which apparently takes place in the adsorptive capacity of the colloidal material on extraction may be the chief source of error in the proposed method of determining the colloidal content of soils, at least when the ratios are based on the quantities of ammonia adsorbed. Extraction seems to render the colloidal material as a rule slightly more adsorptive of dye, slightly less adsorptive of water and considerably less adsorptive of ammonia. This would tend to make the adsorption ratio low by dye, and high by water and ammonia, in proportion to the degree of alteration.

Determinations of the colloidal content of soils based on the dye adsorption ratio, when inaccurate, should be too low as a rule, since the sampling and alteration errors are additive in this direction. In the case of the water and ammonia adsorption ratios the sampling and alteration errors are in opposite directions and, therefore, tend to neutralize each other. The relative accuracies of the water and ammonia adsorption ratios would, therefore, depend on the relative magnitudes of the two possible errors, the ammonia ratio being less affected by the sampling and the water ratio being less affected by the alteration.

Fortunately it was found possible to determine the total quantity of colloidal material in the soil by a method entirely independent of adsorption determinations (Fry, *13*). The method seems to be accurate within a few per cent; hence a direct comparison can be made of the relative accuracies with which the dye, water, and ammonia adsorption ratios represent the quantity of colloidal material in the soil.

If all, or the larger part of, the colloidal material is separated from the soil, the unextracted colloidal material in the washed soil residues can be estimated with considerable accuracy by means of the petrographic microscope as described on page 22. The total quantity of colloid in the soil is thus the sum of the quantity actually separated and the quantities determined microscopically in the soil residues. In Table 10 the quantities of colloid determined in this way are compared with the quantities determined by the uncorrected adsorption ratios, by the adsorption ratios corrected for possible alteration in the colloid produced by extraction, and by the water-adsorption ratio, using an average factor for the water adsorptive capacity of the colloid.

TABLE 10.—*Colloidal content of soils determined by different methods.*

Soil.	Percentage of colloidal material in the soil, indicated by—							
	Uncorrected adsorption ratio $\frac{\text{adsorption per gram soil}}{\text{adsorption per gram colloid}}\times 100$, substance adsorbed being:			Quantity of colloid extracted plus the unextracted colloid estimated microscopically.	Adsorption ratio, corrected for alteration in adsorptive capacity of colloid produced by extraction, substance adsorbed being:			Water adsorption ratio, using factor 0.3 for adsorptive capacity of the colloid.
	Dye.	H_2O.	NH_3.		Dye.	H_2O.	NH_3.	
Cecil clay loam, soil	9.3	18.1	20.6	18.4	11.0	11.2	15.9	14.7
Cecil clay loam, soil (duplicate determination)	8.0	15.6	....	18.3	9.7	12.0	....	14.7
Huntington loam, soil	25.8	24.0	38.5	25.9	25.5	20.4	27.3	17.8
Huntington loam, subsoil	19.8	26.4	36.7	24.5	21.4	23.5	23.9	26.4
Sassafras silt loam, subsoil	19.7	20.8	25.3	23.5	21.1	19.8	20.2	18.9
Sharkey clay, soil	52.8	59.4	66.3	64.7	54.4	58.2	58.8	58.5
Sharkey clay, soil (colloid graded by supercentrifuge)	59.2	65.3	69.6	(1)	45.0	49.6	51.5	66.1
Vega Baja clay loam, soil (colloid graded by supercentrifuge)	69.8	60.7	78.2	72.4	74.0	66.2	75.9	60.2

[1] The quantity of colloid extracted plus the quantity determined microscopically amounted to 59.7 per cent in this sample. It includes the same class of material as the sample above and is, therefore, a duplicate determination. The adsorption ratios given for the Sharkey soil (colloid graded by the supercentrifuge) should not necessarily agree with the ratios for the first sample of Sharkey soil as they may refer to slightly different classes of material, the two sets of ratios being based on different colloidal material; i.e., on material less than 1 micron and on material less than 0.3 micron.

A comparison of the data in columns 2 to 4 with those in columns 6 to 8 shows that discrepancies between the dye, water, and ammonia adsorption ratios disappear for the most part when a correction is applied for the probable alteration in the adsorptive capacity of the colloid produced by extraction. Also, the corrected dye, water, and ammonia ratios agree well in most cases with the quantities of colloid determined by mechanical separation and microscopic observation. This would indicate that the chief element of inaccuracy in the adsorption method of determining the colloidal content of a soil probably lies in the difficulty of separating a sample of colloidal material from the soil without changing its adsorptive capacity.

The low results afforded by the corrected dye and water ratios for the Cecil soil and the low result by the water ratio for the Huntington soil were probably due to the sampling error. Data given in Table 6 support this view. It is apparent that the unextracted colloid of the Cecil soil had an exceptionally low adsorptive capacity for dye and water but not for ammonia as compared with the extracted colloid. A similar condition obtained for the water adsorption capacities of the extracted and unextracted Huntington soil colloids.

It seems evident from a comparison of the values in columns 2 to 4 with those in column 5 that the water adsorption ratio is more likely to show the true amount of colloid in the soil than the dye or ammonia adsorption ratios if no correction is applied for the altered adsorptive capacity of the extracted colloid, at least when the larger part of the extractable colloidal material is taken as a sample.

It was pointed out in a previous paper (Robinson, *26*) that the average water-adsorptive capacity of the colloids extracted from 34 soils, including those given in Table 2, was 0.3 gram water per gram of colloidal material. Since variations in the adsorptive capacity from the mean value were usually not great, it was suggested that an approximate determination of the colloidal material could usually be obtained by dividing the water adsorptive capacity of the soil by the factor 0.3. This average figure for the water-adsorptive capacity of the colloid applies of course to the colloidal material as extracted and not as in the soil. Data given in Table 9, however, indicate that the average adsorptive capacity of the colloids as in the soil would probably be about the same as this factor. Moreover, the average value was that of colloidal material graded by a supercentrifuge which threw out most of the material between 0.3 micron and 1 micron. In column 9 of Table 10, are given the percentages of colloid calculated by the use of this factor. In the case of four soils this method was fairly accurate, but in the case of the Huntington soil the result was considerably too low.

PROCEDURE SUGGESTED.

It would hardly be justifiable to recommend a procedure definite in all its details for determining the colloidal contents of soils by the adsorption method until some of the uncertain features connected with the method have been further investigated. It seems especially important to study further the possible alteration produced by the procedure of separating and concentrating a sample of colloidal material from the soil. Probably also the methods used for determining the adsorptive capacities of the soils and colloids can be improved to some extent. The preservation of samples of soil and colloid so that they will maintain unchanged their adsorptive capacities should be systematically investigated. Miscellaneous data obtained indicate that when the samples are kept in an air-dried condition the adsorptive capacity for malachite green may change in some cases. Also one or two samples of colloid preserved moist underwent a marked alteration in adsorptive capacity for malachite green within a few months' time.

From results obtained thus far the best method of determining the colloidal content of the soil by the adsorption method appears to be as follows: The sample of colloidal material should be separated from the soil as described on pages 20 to 21. Grading of the particles into colloid and noncolloid at a size of 1 micron should be checked by microscopic observation even if the same kind of centrifuge as that described on page 20 is used for the purpose. The dispersed colloidal material may be conveniently collected and concentrated as described on page 8. The adsorptive capacities of the colloid and soil for water vapor may then be determined as described on page 10. According to the data given in Table 10, the ratio of the two adsorptive capacities should, without correction, give very nearly the true amount of colloidal material (particles less than 1 micron in diameter) in the soil. A further check on the results may be obtained by determining the adsorptive capacities of the soil and colloid for dye and ammonia. The dye and particularly the ammonia ratio should, however, be corrected for alteration in the adsorptive capacity of the colloid produced by extraction. To get this corrective factor as calculated on page 28 is a laborious task; it is necessary to determine the adsorptive capacities of the residues left after extraction of the colloidal material, and the quantities of soil residues and of colloid separated must be determined accurately. If a marked disagreement should occur in the corrected ratios, it would presumably be due to the unextractable colloid being particularly low in adsorptive capacity as compared with the colloid extracted, and in this case the ammonia ratio would probably be the highest and nearest the true value.

The method of estimating the colloidal content by actual extraction of a large part of the colloidal material and determination of the remainder unextracted by observation with the petrographic microscope can also be used, but considerable familiarity with microscopical work of this character is necessary to secure accurate results and extraction of much of the colloidal material is a long operation.

The adsorption method of determining soil colloids as proposed is obviously not accurate in the sense that most chemical analyses are, but it is plainly much more accurate than any method of mechanical analysis that has yet been proposed, in view of the fact that the quantities of colloidal matter which we were able to isolate by an especially long continued treatment of the soil (Tables 3 and 4) were only 40 to 60 per cent of the total quantities present (Table 10).

This paper is concerned chiefly with an examination of the adsorption method of estimating colloids, but the quantities of colloid shown by this method to be present in the more important soil types are of interest as enlarging our general knowledge of soils. This is discussed in the following section.

QUANTITY OF COLLOIDAL MATERIAL IN SOILS.

It seems to have been a quite general opinion that soils contain only a small quantity of colloidal material. Gedroiz (*14*) holds that soils contain less than 0.02 per cent of material which will go into colloidal suspension on treatment with water (1 part soil to 5 parts water).[15] Schloesing (*34*) and recently Ehrenberg (*8*, p. 99) state that soils almost never contain more than 2 per cent of colloids. Lyon (*19*), Russell (*29*), and Wiegner (*38*) do not state the amounts of colloidal material that may be expected in soils of different characters. Mellor (*20*) gives the content of colloidal clay, "l'argile colloidale," in Cornish china clay and Devonshire ball clays as being probably something more than 0.005 and 0.05 per cent, respectively.[16]

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[15] Gedroiz makes a distinction between the gel material in the soil and the colloidal material obtained in the water extract.

The data given in the preceding pages show that the total quantity of colloidal material in soils is far greater than many investigators had supposed was present. It is more in accord with the quantities of the Schlamm fraction obtained by Williams (*39*) and the "clay" fraction obtained by Hilgard (*15*).

Naturally views concerning the quantity of colloidal material in soils will vary according to differences of opinion regarding just what soil materials should be classed as colloidal. The older view that the inorganic material in soils consisted of definite mineral particles of all degrees of fineness has lately been modified somewhat. The more general view at the present time is that the mineral particles are coated with a film of colloidal, gelatinous material. Even at the present time, however, the prevalent idea seems to be that in the finer soil fractions mineral fragments of quartz, feldspar, etc., predominate. For instance, Sven Odén (*24*, p. 328) states that: "The true soil colloids are the innumerable fragments of both weathered and unweathered minerals, crystal chips and amorphous substances, which, in a fine state of division, constitute the clay." If the colloidal material in soils were made up entirely of small crystalline particles of such minerals as form the coarser soil particles, there would probably be little difference of opinion regarding the quantity of such material in soils, once the upper limit of colloidal size was agreed upon. The colloid could probably be determined by relatively simple methods of mechanical analysis, since the ultimate particles would be definite and would doubtless readily deflocculate.

Three different lines of evidence, however, indicate that the colloidal material in soils is not composed chiefly of fragments of minerals, at least of such minerals as constitute the larger soil particles. It is apparent from the results given in this paper that merely shaking with water deflocculates only a small amount of colloidal material and that about 50 per cent of the colloidal material in some soils is very resistant to deflocculation or peptization. Fragments of common soil minerals probably would deflocculate readily. Also, adsorption data given in a previous bulletin indicate that the larger part of the colloidal material in soils is not made up of major soil minerals but rather of substances in a gel-like condition. Finally, chemical analyses of colloidal material extracted from some 40 different soils show that chemically the colloidal material is quite different from the larger soil particles (Robinson and Holmes, *27*).

There is every reason to suppose, as Van Bemmelen (*5*), Ehrenberg (*8*), Wiegner (*38*), Rohland (*28*), and others have previously pointed out, that the inorganic colloidal material in soils is similar in nature to artificially prepared gels of silicic acid, aluminum hydroxide, or iron hydroxide. Such materials are, of course, colloidally dispersed when sufficient water is present, but when they are in a partially dry condition the silica, alumina, and iron, may be regarded as constituting the dispersion medium and water or air the dispersed phase; in other words, the particles are colloidal because of the large internal surface produced by their "web" or "brush-heap" structure.[17] Obviously macroscopic particles of such material have much the same properties and are just as truly colloidal as particles a micron or less in size. Data given in Table 6 show that lumps of soil colloids from 1 to 50 microns or so in diameter may in some instances have just as high an adsorptive capacity as the material which is dispersed into particles of 0.3 micron or less in size (adsorptive capacities of Vega Baja soil residues, Table 6.) If these lumps contain crystalline or discrete particles, the particles are so small that they can not be recognized as crystalline by the petrographic microscope. i. e., they must be at any rate less than 1 micron in diameter. Under the ultramicroscope they appear to consist of aggregates of particles less than a micron in size.

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[16] However, Mellor points out as a significant fact that when these quantities of colloidal material are extracted from the clays no detectable difference in plasticity is noted.

Obviously a soil in the air-dried condition contains practically no colloidal material in the sol condition as there is not sufficient water present to act as the dispersing medium. Also, as pointed out in the first part of this paper, the amount of colloidal material that is present as a sol when the soil is merely agitated once in a certain volume of water is very indefinite and uncharacteristic of the total quantity of colloidal material in the soil which is capable of assuming this form. Many of the low estimates of the colloidal content of soils, such as that of Gedroiz (*14*), are based on determinations of this kind.

It must be recognized that much of the material in soils which has been classed as colloidal in this paper does not have a definite size of ultimate or "primary" particle in the sense that a single crystal has a definite or ultimate size. Size as ordinarily apparent without a consideration of structure means little.[18] Lumps of partially dry gels may appear as large particles, yet in the presence of sufficient water they may disperse into particles or "droplets" of submicroscopic size. The exact size of particles into which such material will disperse depends chiefly upon the conditions of dispersion. A single crystalline particle, however, is definite as regards size. Heretofore, recognition of the gel-like material in soils as colloidal has been dependent almost entirely upon conversion of the gel into the sol condition, where the particles or aggregates are small. This is an uncertain method. In this study the gel material has been recognized partly in this way, partly through its adsorptive capacity, and partly by microscopic observation of structure.

Placing the maximum quantity of colloidal material in soils at 2 per cent is obviously wrong, even if we were to classify as colloids only that material which could readily be deflocculated or peptized into particles of submicroscopic size. Data given in Table 3 show that from 6 to 38 per cent of such material was isolated from five soils, by no more drastic treatment than rubbing the soil with water containing a trace of ammonia. The probable reason for the low results obtained by other investigators was given in the first part of this paper.

If the definition of colloidal soil material given in the first part of this paper be accepted, it can be seen from Table 10 that six different soils contained from 17 to 70 per cent of colloids. These values, moreover, were arrived at by two independent methods of determination.

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[17] For a development of this idea, see Freundlich (*10*, p. 905–908).

[18] Ormandy (*25*) points out that the size of a particle of ball clay is dependent on the time it is in contact with water and on the volume of water; hence the system of mechanical analysis suggested by Professor Odén measures nothing definite when dealing with clay.

Some idea of the quantities of colloids that are present in different kinds of soils may be gained from the data given in Table 2. The quantities indicated by the water-adsorption ratios in this table are probably the most accurate; since data given in Table 10 show that when no correction is applied to the ratio

$$\frac{\text{adsorption per gram soil}}{\text{adsorption per gram colloid}}$$

for alteration in the adsorptive capacity of the colloid produced by extraction, the results obtained by water adsorption are likely to be the most accurate. The values given in Table 2 are calculated on the basis of a sample of the colloidal material which was graded by the supercentrifuge; that is, the dispersed particles appeared to be below 0.3 micron in diameter. Uncorrected water adsorption ratios calculated on the basis of a sample of colloidal material graded in this way are little different as a rule from uncorrected ratios calculated on a sample of colloidal material graded with one micron as the largest diameter of the colloidal particles. This is apparent from the data given in Table 11. Hence the water adsorption ratios given in Table 2 probably indicate fairly closely as a rule the true percentages of colloidal material as defined in the first part of this paper.

TABLE 11.—*Percentages of colloidal material in soils shown by adsorption ratios based on colloidal material below 0.3 micron and below 1 micron.*[1]

Soil.	Adsorption ratio ×100 based on 0.3 micron colloidal material, substance adsorbed being—			Adsorption ratio ×100 based on 1 micron colloidal material, substance adsorbed being—			Percentage colloidal material less than 1 micron present by extraction and microscopical determination.
	Dye.	H_2O.	NH_3.	Dye.	H_2O.	NH_3.	
Cecil clay loam, soil	10	10	15	9	17	21	18
Huntington loam, soil	14	23	33	26	24	39	26
Huntington loam, subsoil	12	20	30	20	26	37	25
Sassafras silt loam, subsoil	13	19	22	20	21	25	24
Sharkey clay, soil	59	65	70	53	59	66	65

[1] Values taken from Tables 2 and 10.

It will be seen that the uncorrected water and ammonia adsorption ratios based on the two samples of colloidal material agree quite well in the case of all soils except the Cecil.[19]

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[19] In other words, the adsorptive capacities for water and ammonia of the extracted, supercentrifuge and 1-micron graded colloids were practically the same. (Compare also data on adsorptive capacities of colloids in Tables 1 and 3 with similar data in Table 4). The 1-micron colloid as a rule is a little lower in adsorptive capacity for water and ammonia and markedly lower in adsorptive capacity for dye than the supercentrifuge colloid. This may well be due to the inclusion in the 1-micron colloid of a certain amount of common soil mineral particles ranging between 0.3 micron and 1 micron in diameter which would probably have a distinctly smaller adsorptive capacity than the gel-like colloidal material, especially for malachite green. A previous investigation showed that prepared common soil mineral particles below 1 micron in size were low in adsorptive capacity, particularly for dye, as compared with the average colloidal material graded by the supercentrifuge. (Anderson, *1*.) It is possible, however, that the difference in adsorptive capacities of the two samples of colloidal material is due simply to different degrees of alteration in adsorptive capacity produced by slightly different methods of preparing the samples. Unfortunately it was not possible to obtain data on the possible extent to which the colloids reported in Table 1 may have been altered by extraction.

The water adsorption ratios indicate that the 32 soils reported in Table 2 contain from 6 to 61 per cent of colloidal material, the 6 different loam soils averaging 20 per cent of colloid. In the case of many soils the quantity of colloidal material present exceeds the percentage of "clay" shown by the old system of mechanical analysis, as practiced in this bureau.[20] Thirty of the soils contain an average of 19 per cent clay by mechanical analysis and 23 per cent of colloid by the water adsorption ratio. The widest difference occurs in the case of the Sharkey soil, with 36 per cent of clay as compared with 61 per cent of colloidal material. The clay fraction is supposed to contain all particles below 5 microns in diameter, but it has been pointed out by Davis (*7*) and it is evident from the results reported in this paper that aggregates of colloidal material above clay size are fairly abundant in the soil.

The data in this paper show that, on the whole, soils contain only a slightly larger amount of the finest material than has heretofore been reported as "clay" (particles below 0.005 millimeter in diameter). The old clay fraction of a soil then, except in the case of certain very heavy soils, gave, as a rule, a rough idea of the quantity of finest material in the soil. It is apparent, however, from the data reported here that the clay fraction did not contain all the finest material and that most of the material which was included in this fraction is much finer than had been thought and is moreover preponderantly of a quite different character from the mineral grains present in the fractions of larger particles.

The old view that the soil consists chiefly of mineral grains of varying sizes coated possibly with a thin film of colloidal material obviously needs to be modified. If 6 to 70 per cent of the soil consists of colloidal material of a gel-like nature, this material evidently is not present as a film only.

It seems evident that the large quantity of colloidal material in the soil must be as much a determining factor of the chemical behavior as of the physical character of a soil. And since the colloidal material consists chiefly of the more insoluble products formed from the decomposition of the soil minerals, it should constitute one of the more important criteria for the classification of soils.

A knowledge of the total amount of colloidal material present in soils is only a preliminary step toward studying the colloids and investigating further the chemical and physical processes going on in the soil. Information concerning the different kinds and conditions of the colloidal materials present in a given soil is also needed. Evidence of this need is given in the preceding pages. The mixed colloids extracted from one soil, for instance, were seven times as adsorptive for malachite green and three times as adsorptive for ammonia as the colloids extracted from another soil. Furthermore, the mixed colloidal material in a given soil appears to be present in more than one physical condition, judging from the varying ease with which parts of it are brought into suspension.

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[20] Mechanical analyses of 30 of the soils were kindly made by A. A. Riley and J. B. Spencer according to the methods described in Bulletin 8 of the Bureau of Soils (Fletcher, *9*).

SUMMARY.

The noncolloidal soil constituents are defined in this paper as the distinctively mineral particles above 1 micron in diameter. The following are classified as colloidal constituents: All the organic matter, inorganic material dispersing into particles below 1 micron in diameter, and aggregates of particles less than 1 micron in diameter.

The earliest method of determining the colloidal material in soils consisted in actually separating the material from the rest of the soil. The probable error in this method is the difficulty of obtaining a complete deflocculation or peptization of the colloidal material. This error is enormous in some rapid methods recently suggested. Adsorption methods previously proposed probably do not indicate in most cases even the relative colloidal contents of soils, since they do not include a determination of the adsorptive capacity of the kind of colloidal material present.

The adsorption method of determining the colloidal content of soils investigated in this paper involves determinations of the adsorptive capacities both of the soil and of colloidal material extracted from the soil. The ratio of the two adsorptive capacities multiplied by 100 is taken as giving the percentage of colloidal material in the soil. Tests of this method on 32 soils are reported, the percentages of colloidal material being calculated from the adsorptions of malachite green, water, and ammonia.

The colloidal materials extracted from different soils vary greatly, in their adsorptive capacities for malachite green and ammonia, but are much more constant in their adsorptive capacity for water.

In the case of 13 soils the percentages of colloid calculated from the adsorptions of malachite green, water, and ammonia agree; in the case of 14 soils the percentages indicated by the adsorptions of two of the substances agree but disagree with the percentage indicated by the adsorption of the third substance; and in the case of 5 soils different percentages of colloid are indicated by the adsorption of all three substances, malachite green, water, and ammonia.

The two most probable sources of error in the adsorption method of determining the colloidal content of a soil appear to be the difficulty of extracting a sample of colloidal material which is exactly representative in adsorptive capacity of all the colloidal material in the soil, and the possibility of a change taking place in the adsorptive capacity of the colloid on extraction. These two possible sources of error are investigated in the case of several soils.

The adsorptive capacity of a small sample of extracted colloidal material differs by about 10 per cent from the adsorptive capacity of all the colloidal material which is extractable by the methods employed. However, the colloidal material which can not be extracted has, in many soils, a much lower adsorptive capacity than that which is extractable.

Evidence is presented which indicates that the colloidal material has a somewhat different adsorptive capacity after extraction than it has in the untreated soil. The data indicate that the colloidal material of most soils in its extracted condition is slightly more adsorptive of malachite green, slightly less adsorptive of water vapor and considerably less adsorptive of ammonia than in its condition in the untreated soil.

The errors of sampling and of probable alteration of the colloidal material vary in magnitude in different soils. They are additive as a rule in the case of dye adsorption and tend to balance each other in the case of water or ammonia adsorption.

The accuracy of the adsorption method is checked by comparing in the case of six soils the quantities of colloid shown by this method with the quantities shown by a gravimetric and microscopical method. When the adsorption ratios are corrected for possible alteration in adsorptive capacity of the colloid produced by extraction, the percentages of colloidal material indicated by the adsorptions of malachite green, water, and ammonia agree well in nearly all cases with the percentages of colloid determined gravimetrically and microscopically. When no correction is applied for alteration in adsorptive capacity of the colloid, the ratio obtained by the adsorption of water in most cases is more accurate than the dye or ammonia ratio, and approaches the true value closely.

A general procedure is suggested for estimating the quantity of colloidal material present in a soil from the relative adsorptive capacities of the soil and of colloidal material extracted from the soil.

It is pointed out that the wide discrepancy between the estimates of the colloid contents of soils given out by various investigators is due in part to differences in definition of "soil colloids" and in part to faulty methods. The 32 soils selected for this investigation contained from 6 to 70 per cent of colloidal material as defined in this paper. Placing the maximum quantity of colloidal material in soils at 2 per cent is obviously wrong, even if soil colloids are defined to include only that material which is dispersed into particles of submicroscopic size. As much as 38 per cent of such material has actually been isolated from a heavy soil. The probable reason is given for the low results obtained by certain investigators.

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